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Highly Stereoselective Syntheses of Alkenylsilanes and Germanes Utilizing Cyclobutyl Ketones

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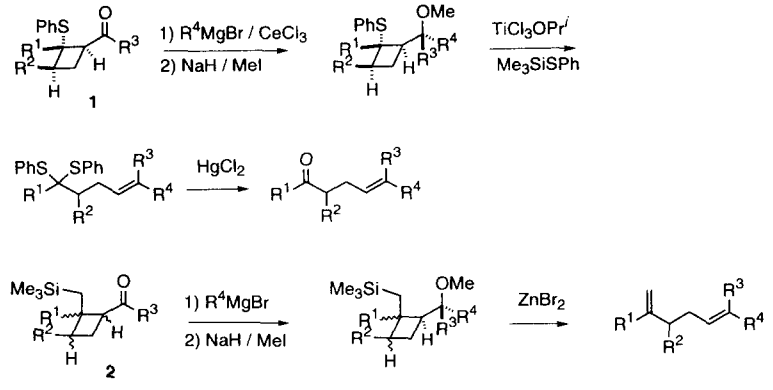
Abstract: (*E*)-Alkenylsilanes were synthesized with high stereoselectivity by the diastereoselective addition of the dimethylphenylsilyllithium to the *trans*-2-phenylthiocyclobutyl ketones and the Lewis acid-promoted stereospecific ring opening reactions of the resulting cyclobutanemethanol derivatives. (*E*)-1,5-Disubstituted-1,5-dienylsilanes and germanes were also produced stereoselectively by the similar zinc salt-catalyzed ring opening reaction of α-dimethylphenylsilyl- or α-triethylgermyl-1-[2-(trimethylsilylmethyl)cyclobutane]methanol derivatives. © 1997 Elsevier Science Ltd.

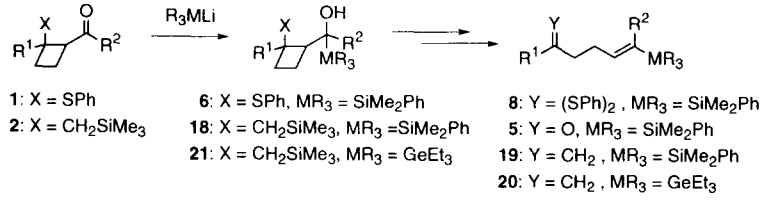
The stereoselective construction of carbon-carbon double bond is one of the most important processes in the synthesis of some natural products, and a variety of methods have been investigated. Alkenylsilanes are the useful synthetic precursors of alkenes since they are converted stereospecifically to the corresponding alkenyl halides[1] and alkenylboranes[2] with retention or inversion of configuration. The stereospecific intramolecular carbon-carbon bond formations with retention of configuration were also reported.[3] Stereoselective synthesis of alkenylsilanes have been achieved by silation of alkenylmetals,[4] silacupration[5] or hydrosilation[6] of terminal alkynes, and hydrometallation[7] or carbometallation[8] of alkynylsilanes.

In the course of study on the syntheses and reactions of cyclobutanes,[9] we have recently developed the versatile methods for the highly stereoselective preparation of various trisubstituted olefins utilizing *trans*-2-phenylthiocyclobutyl ketones **1**[10] and 2-(trimethylsilylmethyl)cyclobutyl ketones **2**[11] (Scheme 1). The former method includes the following steps; 1) the addition of Grignard reagent to **1**, 2) the transformation of the resulting alcohol to the methyl ether, 3) its reaction with phenylthiotrimethylsilane promoted by trichloroisopropoxytitanium, and 4) hydrolysis of the thioacetal formed with mercury(II) chloride. With a similar approach, 1,1,5-trisubstituted 1,5-dienes were stereoselectively synthesized by the zinc bromide catalyzed 1,4-elimination of 1-methoxymethyl-2-(trimethylsilylmethyl)cyclobutanes. It was assumed that the high stereoselectivity of these transformations were accomplished by a combination of the diastereoselective addition of Grignard reagents to **1** or **2** and the stereospecific ring opening reaction of the resulting cyclobutanemethanol derivatives.

On the basis of the above results, we have investigated stereoselective synthesis of alkenylsilanes utilizing cyclobutyl ketones **1** and **2** as starting materials. Our approach is outlined in Scheme 2 which consists of the addition of triorganosilyllithium to **1** or **2**, and the following ring opening reaction of the adduct. The preparation of alkenylgermanes using the cyclobutyl ketones **2** and triethylgermyllithium was also investigated. Alkenylgermanes have been found to be useful precursors for the stereoselective synthesis of alkenyl halides.[12]



Scheme 1

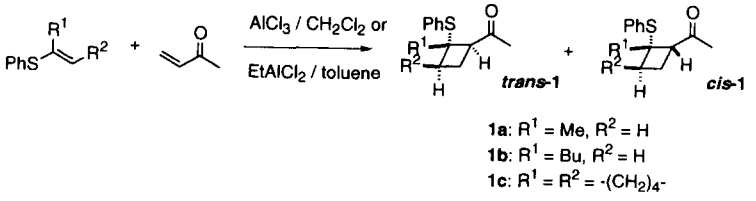


Scheme 2

RESULTS AND DISCUSSION

*Preparation of 2-phenylthiocyclobutyl and 2-(trimethylsilylmethyl)cyclobutyl ketones **1** and **2***

The starting 2-phenylthiocyclobutyl ketones **1a-c** were easily prepared in good yields by the aluminum chloride-catalyzed [2+2] cycloaddition of alkenyl sulfides with methyl vinyl ketone developed by us[13] (Scheme 3, Table 1). In all the cases examined, the stereoisomers ***trans*-1**, in which an acetyl group was *trans* to a phenylthio group, predominated and they were isolated easily by silica gel column chromatography. The cyclobutyl ketones ***trans*-1d** and **e** were synthesized by the reactions of the lithium enolate of ***trans*-1c** with methyl iodide and prenyl bromide in 90% and 78% yields, respectively (Scheme 4).

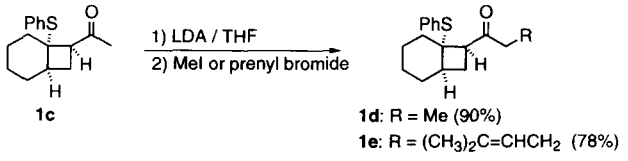


Scheme 3

Table 1. [2+2] Cycloaddition of Alkenyl Sulfides and Methyl Vinyl Ketone

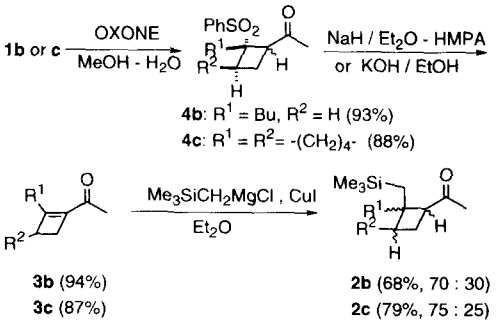
Alkenyl sulfide	Lewis acid (equiv)	Solvent	Temp (°C)	Time (min)	Product[a] (Yield/%)	*trans* : *cis*[b]
	$AlCl_3$ (0.2)	CH_2Cl_2	-78	20	**1a** (91)	89 : 11[c]
	$AlCl_3$ (0.2)	CH_2Cl_2	-78	30	**1b** (83)	85 : 15
	$EtAlCl_2$ (0.2)	toluene	-65	120	**1c** (73)[d]	89 : 11

a The stereochemistry of the cyclobutane **1** was determined by NOE experiment. *b* Determined by NMR spectroscopy. *c* Based on the isolated yields. *d* 1-Phenylthiocyclohexene (15%) was recovered.

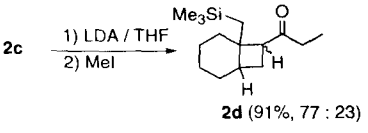


Scheme 4

The other starting materials, methyl 2-(trimethylsilylmethyl)cyclobutyl ketones **2b** and **c**, were prepared from 2-phenylthiocyclobutyl ketones **1b** and **c** in three steps (Scheme 5). The cyclobutenyl ketones **3** were obtained by the oxidation of **1** with potassium peroxymonosulfate (OXONE®), followed by the base-promoted elimination of the resulting sulfones **4**. The copper(I) iodide-assisted addition of trimethylsilylmethylmagnesium chloride to **3** afforded **2** as mixtures of stereoisomers in good yields. Preparation of **2d** was performed by the methylation of the lithium enolate of **2c** with methyl iodide in 91% yield (Scheme 6). The stereoisomeric mixtures of **2b-d** thus obtained were employed for the further reactions without separation of the stereoisomers.



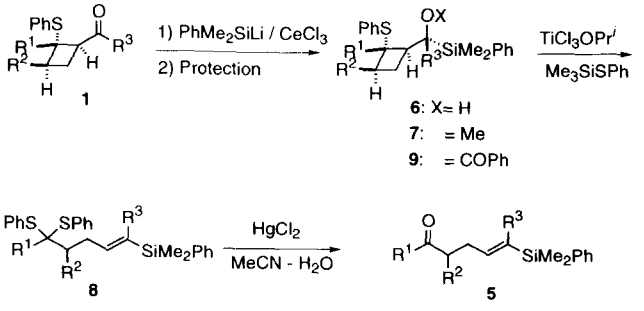
Scheme 5



Scheme 6

Synthesis of alkenylsilanes using 2-phenylthiocyclobutyl ketones 1

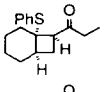
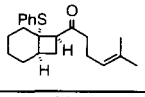
First the preparation of δ-dimethylphenylsilyl-γ, δ-unsaturated ketones **5** using 2-phenylthiocyclobutyl ketones **1** was examined (Scheme 7). It was observed by NMR measurement of the crude product that the adduct **6a** was formed when 1-acetyl-2-methyl-2-phenylthiocyclobutane **1a** was treated with 1.5 equiv of dimethylphenylsilyllithium[14] in THF at -78 °C. However, it was also confirmed that a substantial amount of the starting ketone **1a** remained unreacted. On the other hand, **1a** was completely transformed to the α-silyl alcohol **6a** when the reaction was carried out in the presence of cerium(III) chloride.[15]



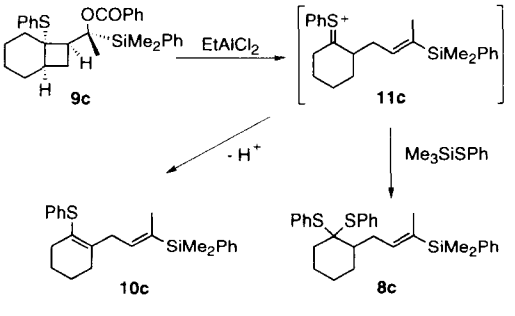
Scheme 7

After protection of the hydroxyl group, the Lewis acid-catalyzed ring opening reaction was performed. The methyl ether **7a** was prepared in 41% overall yield from **1a**. The treatment of **7a** with phenylthiotrimethylsilane in the presence of trichloroisopropoxytitanium(IV) at -78~0 °C for 27 h gave the thioacetal **8a** in 47% yield as a single stereoisomer. The titanium(IV)-promoted reaction of the benzoate **9a**, produced in 68% overall yield by the successive treatment of **6a** with butyllithium and benzoyl chloride, also gave **8a** in 63% yield. The better yield of **8a** (73%) was obtained when using ethylaluminum dichloride as a catalyst. The thioacetal **8a** was easily transformed to (*E*)-vinylsilane **5a** in 95% yield by hydrolysis with mercury(II) chloride in acetonitrile-H_2O. In a similar manner, (*E*)-vinylsilanes ***E*-8c** and **d** were prepared with high stereoselectivity as shown in Table 2. In the case of **1e** possessing a relatively large acyl group, the formation of a small amount of the *Z*-isomer was observed (Entry 6). The fact that the alkenyl sulfide **10c** was produced as a by-product in the ethylaluminum dichloride-promoted reaction of **9c** suggests that the reaction proceeds through the thionium ion intermediate **11c** as depicted in Scheme 8.

Table 2. Preparation and Ring Opening Reaction of (2-Phenylthiocyclobutyl)methyl Benzoate **9**.

Entry	Cyclobutyl ketone **1**	Benzoate **9** (Yield/%)	Thioacetal **8** Lewis acid	Temp (°C)	Time (h)	Yield (%)	Alkenylsilane **5** (Yield/%)	*E* : *Z*[a]
1		**9a**(68)	$EtAlCl_2$	-78~0	7	**8a**(73)	**5a**(95)	100 : 0
2	***trans*-1a**		$TiCl_3OPr^i$	-45~0	5	**8a**(63)		100 : 0
3		**9c**(69)	$EtAlCl_2$	-20	0.67	**8c**(46)[b]	**5c**(78)	100 : 0
4	***trans*-1c**		$TiCl_3OPr^i$	-78~-45	3.5	**8c**(76)		100 : 0
5	 ***trans*-1d**	**9d**(53)	$TiCl_3OPr^i$	-78~-30	28	**8d**(64)	**5d**(92)	100 : 0
6	 ***trans*-1e**	**9e**(57)	$TiCl_3OPr^i$	-78~-40	23	**8e**(50)	**5e**(80)	90 : 10

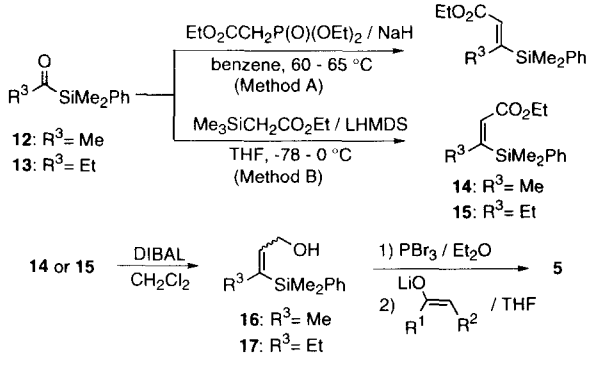
[a] Determined by NMR spectroscopy. [b] The cyclohexenyl sulfide **10c** was isolated in 29% yield.



Scheme 8

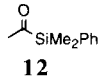
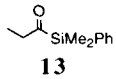
The stereochemistry of alkenylsilanes **5** described above was determined by the comparison with the authentic samples of *E*- and *Z*-isomers. These compounds were prepared by the reaction sequences shown in Scheme 9, the first steps of which were originally developed for the stereoselective preparation of trisubstituted olefins. Acylsilanes **12** and **13** were treated with sodium salt of diethyl ethoxycarbonylmethylphosphonate in benzene (Method A) to afford (*E*)-β-dimethylphenylsilyl-α,β-unsaturated esters ***E*-14** and **15** predominantly.[16] The corresponding *Z*-isomers ***Z*-14** and **15** were obtained by the treatment of **12** and **13** with lithium enolate of ethyl trimethylsilylacetate in THF at -78~0 °C (Method B).[17] By these methods both stereoisomers of **14** and **15** were obtained in around 90% stereoselectivity, and the results were summarized in Table 3.

After the stereoisomers of **14** and **15** were separated each other by preparative TLC, they were reduced with diisobutylaluminum hydride in dichloromethane at -78 °C to afford the corresponding allylic alcohols **16** and **17**. Their bromination with phosphorus tribromide followed by the treatment with lithium enolates gave the authentic (*E*)- and (*Z*)-δ-dimethylphenylsilyl-γ,δ-unsaturated ketones **5a**, **b**, **c**, and **d**. Their chemical shifts of vinyl protons β to a silyl group are summarized in Table 4; the vinyl protons of *E*-isomers are always upfield compared with those of *Z*-isomers. The configurations of two stereoisomers ***E*-** and ***Z*-5e** were assigned on the basis of their chemical shifts of vinyl protons.



Scheme 9

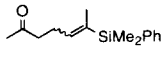
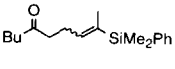
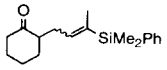
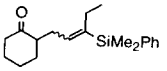
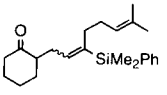
Table 3. Preparation of β-Dimethylphenylsilyl-α,β-unsaturated Esters **14** and **15**

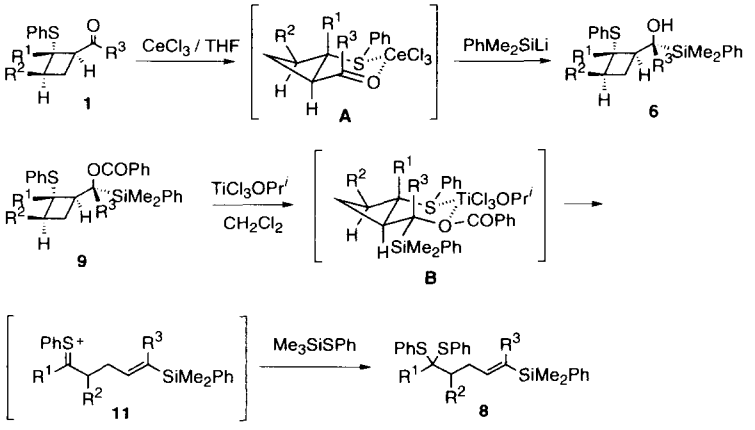
Acylsilane	Method[a]	Product (Yield/%)[b]	*E* : *Z*[c]
 **12**	A	**14** (72)	96 : 4
	B	**14** (81)	13 : 87
 **13**	A	**15** (89)	91 : 9
	B	**15** (78)	10 : 90

a Method A: NaH (1 equiv) / $EtO_2CCH_2P(O)(OEt)_2$ (1 equiv) / benzene / 60~65 °C; Method B: lithium hexamethyldisilazide (LHMDS) (1.2 equiv) / $Me_3SiCH_2CO_2Et$ (1.2 equiv) / THF / -78~0 °C. *b* The stereochemistry of the esters **14** and **15** was determined by NOE experiment. *c* Determined by NMR spectroscopy.

The stereoselectivity of the transformation of **1** into **8** is well explained by the transition states similar to those proposed to the synthesis of γ,δ-unsaturated ketones from **1** and Grignard reagents.[9] The silyl anion attacks from the less-hindered side of the rigid six-membered cyclic chelate **A** formed from **1** and cerium(III) chloride to yield the alcohol **6** having the stereochemistry depicted in Scheme 10. The titanium(IV)-promoted ring opening reaction proceeds through the most stable chair-preferred cyclic transition state **B** to give the *E*-alkenylsilane **8**. Since the same stereoselectivity was observed in the reactions using ethylaluminum dichloride, the reaction might be proceed through the transition state with the conformation similar to **B**.

Table 4. The Chemical Shifts of Vinyl Protons β to a Silyl Group of Vinylsilanes **5**.

Vinylsilane **5**		Configuration	δ (in $CDCl_3$)	Configuration	δ (in $CDCl_3$)
	**5a**	*E*	5.73	*Z*	5.95-6.07
	**5b**	*E*	5.73	*Z*	5.95-6.07
	**5c**	*E*	5.70-5.84	*Z*	6.00-6.12
	**5d**	*E*	5.65-5.81	*Z*	5.99-6.06
	**5e**	*E*	5.69-5.83	*Z*	5.98-6.09

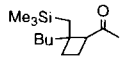
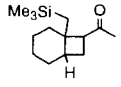
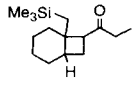


Scheme 10

Synthesis of alkenylsilanes using 2-(trimethylsilylmethyl)cyclobutyl ketones **2**

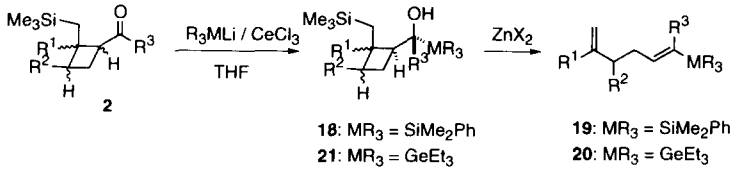
The reaction of 1-acetyl-2-butyl-2-(trimethylsilylmethyl)cyclobutane (**2b**) with dimethylphenylsilyllithium in the presence of cerium(III) chloride at -78 °C gave α-silylcyclobutanemethanol **18b**. Without any purification and protection of the hydroxyl group, **18b** was then treated with zinc bromide in dichloromethane to afford (*E*)-2-butyl-6-(dimethylphenylsilyl)hepta-1,5-diene (**19b**) with complete stereoselection in 56% yield (Scheme 11). Similarly several (*E*)-1,5-disubstituted hexa-1,5-dienylsilanes **19** were prepared in good overall yields (Table 5). A similar reaction sequence using triethylgermyllithium[18] also gave (*E*)-alkenylgermanes **20** via α-germylcyclobutanemethanols **21**. In the case of the ring opening reaction of **21d**, the use of longer reaction time improved the yield of **20d** though its stereoisomeric purity was slightly diminished (Entry 11). The high stereoselectivity of these reactions is of special interest because the stereoisomeric mixtures were used as starting materials. At present we assume that the high *E* selectivity is explained by the attack of organometallic species to 2-(trimethylsilylmethyl)cyclobutyl ketone **2** from the less hindered side of the conformer **C**, in which the repulsion between R^3 in the acyl moiety and the substituents on the cyclobutane ring is minimized (Scheme 12). The subsequent ring opening reaction proceeds through the chair-preferred transition state **D**, **E**, or **F** depending on the configuration of cyclobutane moiety. Considering that the stereoselectivity of this reaction is higher than that

Table 5. Preparation of (*E*)-1,5-Disubstituted Hexa-1,5-dienylsilanes **19** and Germanes **20**

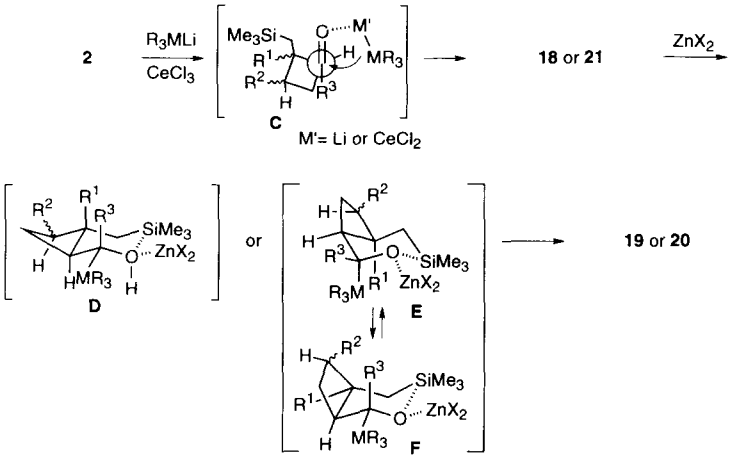
Entry	Cyclobutyl ketone **2**	R_3MLi	ZnX_2	Time (h)	Product (Yield/%)	$E : Z^a$
1		$PhMe_2SiLi$	$ZnBr_2$	2	**19b** (56)	100 : 0
2		Et_3GeLi	$ZnBr_2$	3	**20b** (52)	100 : 0
3	**2b**	Et_3GeLi	$ZnCl_2$	1.75	**20b** (54)	100 : 0
4		$PhMe_2SiLi$	$ZnBr_2$	1.5	**19c** (67)	100 : 0
5		$PhMe_2SiLi$	$ZnCl_2$	0.75	**19c** (69)	100 : 0
6		Et_3GeLi	$ZnBr_2$	3	**20c** (55)	100 : 0
7	**2c**	Et_3GeLi	$ZnCl_2$	3.5	**20c** (60)	100 : 0
8		$PhMe_2SiLi$	$ZnBr_2$	3	**19d** (53)	100 : 0
9		$PhMe_2SiLi$	$ZnCl_2$	4	**19d** (45)	100 : 0
10		Et_3GeLi	$ZnBr_2$	14	**20d** (45)	100 : 0
11	**2d**	Et_3GeLi	$ZnBr_2$	26	**20d** (59)	97 : 3
12		Et_3GeLi	$ZnCl_2$	10	**20d** (38)	100 : 0

a Determined by NMR spectroscopy.

observed in the preparation of trisubstituted olefins using **2** and Grignard reagents,[11] it is clear that an increase in the steric bulk of the attacking organometallic species enhances the *E*-stereoselectivity.

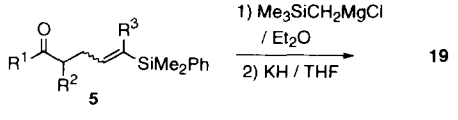


Scheme 11



Scheme 12

The authentic alkenylsilanes **19** used for assignment of configuration were prepared by the reaction of δ-dimethylphenylsilyl-γ,δ-unsaturated ketones **5** with trimethylsilylmethylmagnesium chloride in refluxing ether followed by the treatment of the resulting β-hydroxysilanes with potassium hydride in THF at 30 °C (Scheme 13). The authentic alkenylgermanes **20** were also synthesized by a similar reaction sequences using acylgermanes **22** and **23** as starting materials (Scheme 14, Table 6).

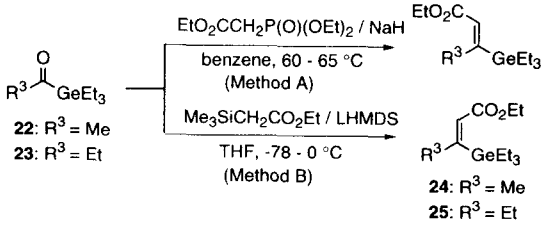


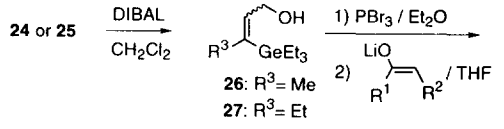
Scheme 13

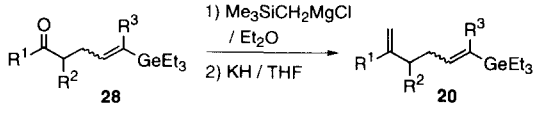
Table 6. Preparation of β-Triethylgermyl-α,β-unsaturated Esters **24** and **25**

Acylgermane	Method[a]	Product (Yield/%)[b]	$E : Z$[c]
 **22**	A	**24** (79)	97 : 3
	B	**24** (80)	13 : 87
 **23**	A	**25** (44)	92 : 8
	B	**25** (68)	10 : 90

a Method A: NaH (1 equiv) / $EtO_2CCH_2P(O)(OEt)_2$ (1 equiv) / benzene / 60~65 °C; Method B: LHMDS (1.2 equiv) / $Me_3SiCH_2CO_2Et$ (1.2 equiv) / THF / -78~0 °C. *b* The stereochemistry was determined by NOE experiment. *c* Determined by NMR spectroscopy.







Scheme 14

CONCLUSION

The reactions of *trans*-2-phenylthiocyclobutyl ketones ***trans*-1** and 2-(trimethylsilylmethyl)cyclobutyl ketones **2** with dimethylphenylsilyllithium followed by the Lewis acid-promoted ring opening reactions provide the useful synthetic methods for the highly stereoselective preparation of (*E*)-alkenylsilanes **5** and **19**. (*E*)-Alkenylgermanes **20** can be also prepared by similar procedures using the cyclobutyl ketones **2** and triethylgermyllithium.

EXPERIMENTAL SECTION

General.

^1H (200MHz, 270MHz, 500MHz) and ^{13}C (125MHz) NMR spectra were recorded on a Jeol FX-200, GX-270, A-500 using $CDCl_3$ as a solvent. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^1H and from deuteriochloroform for ^{13}C spectroscopies. IR spectra were recorded on a Jeol Diamond-20 FT-IR spectrometer; absorptions are reported in cm^{-1}. Elemental analyses were performed on a Perkin Elmer 2400II. Melting points were recorded on a Yanaco MP-S3 apparatus. Boiling points are uncorrected. All the reactions were performed under an argon atmosphere in dried glassware. For preparative thin layer chromatography and column chromatography, Wakogel B-5F and Merck Si 60 were used as adsorbents, respectively. THF was distilled from sodium and benzophenone under argon immediately before use. Dichloromethane was distilled from calcium hydride under argon immediately before use. Ether was distilled and dried over sodium. Toluene and benzene were distilled and dried over molecular sieves 4A. Aluminum chloride was purified by sublimation. 2-Phenylthioprop-1-ene and 2-phenylthiohex-1-ene were prepared by the alkylation of 1-(phenylthio)vinyllithium[19] with iodomethane and 1-iodobutane in 67 and 65% yields, respectively. 1-Phenylthiocyclohexene was prepared from cyclohexanone by the method reported by Liebeskind et al.[20]

Preparation of alkenylsilanes and alkenylgermanes utilizing cyclobutyl ketones

Preparation of (1R*, 2S*)-2-methyl-2-phenylthiocyclobutyl methyl ketone (*trans*-1a). To a dichloromethane (200 ml) suspension of $AlCl_3$ (2.57 g, 19.3 mmol) was added a dichloromethane (150 ml) solution of 2-phenylthioprop-1-ene (14.46 g, 96.3 mmol) and methyl vinyl ketone (9.6 ml, 116 mmol) dropwise over 15 min at -78 °C. After stirring for 20 min, dry ether (190 ml) and a saturated $NaHCO_3$ aqueous solution (300 ml) was successively added with vigorous stirring. The insoluble materials were filtered off through celite and organic layer was separated. The aqueous phase was back-extracted with dichloromethane (300 ml) and the combined organic layers were dried over Na_2SO_4. The extracts were concentrated under reduced pressure and the purification was accomplished by silica gel column chromatography using hexane-AcOEt (95 : 5) as an eluent to give ***trans*-1a** (17.17 g, 81%) and the (1R*, 2R*)-isomer (***cis*-1a**), (2.11 g, 10%). ***trans*-1a**: IR (neat) 3074, 2966, 2866, 1716, 1583, 1475, 1439, 1362, 1244, 1182, 752, 706, 696; ^1H NMR 1.33 (s, 3H), 1.53-1.90 (m, 2H), 2.14 (s, 3H), 2.05-2.37 (m, 2H), 3.26 (t, *J*=8.1 Hz, 1H), 7.35-7.45 (m, 3H), 7.50-7.60 (m, 2H); ^{13}C NMR 15.84, 22.02, 29.73, 32.76, 52.82, 54.19, 128.85, 128.89, 132.00, 136.36, 206.39. Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.79; H, 7.39. ***cis*-1a**: IR (neat) 3059, 2956, 2857, 1713, 1583, 1475, 1439, 1358, 1184, 752, 706, 694; ^1H NMR 1.66 (s, 3H), 1.80-1.96 (m, 2H), 2.16 (s, 3H), 2.02-2.19 (m, 1H), 2.36-2.62 (m, 1H), 3.20 (t, *J*=8.4 Hz, 1H), 7.23-7.34 (m, 3H), 7.39-7.52 (m, 2H); ^{13}C NMR 17.64, 29.98, 30.63, 32.51, 53.43, 57.77, 128.30, 128.55, 131.95, 135.79, 206.32. Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.59; H, 7.35.

In a similar manner, a stereoisomeric mixture of 1-acetyl-2-butyl-2-phenylthiocyclobutane (**1b**) was prepared using 2-(phenylthio)hex-1-ene and methyl vinyl ketone.

1-Acetyl-2-butyl-2-phenylthiocyclobutane (1b): IR (neat) 3059, 2956, 2860, 1707, 1583, 1473, 1439, 1358, 1178, 750, 706, 696; ^1H NMR 0.92 (t, *J*= 7.3 Hz, 2.55H), 0.95 (t, *J*= 7.3 Hz, 0.45H), 1.23-1.43 (m, 3H), 1.46-1.66 (m, 3H), 1.66-1.95 (m, 2H), 1.95-2.11 (m, 1H), 2.06 (s, 2.55H), 2.13 (s, 0.45H), 2.11-2.26 (m, 1H), 3.21-3.26 (m, 0.15H), 3.29 (t, *J*= 8.7 Hz, 0.85H), 7.23-7.46 (m, 3H), 7.53-7.61 (m, 2H); ^{13}C NMR 14.00, 14.06, 15.92, 17.65, 22.70, 22.95, 26.37, 27.02, 28.89, 30.17, 30.47, 30.56, 33.76, 41.52, 54.68, 55.94, 57.38, 58.18, 128.31, 128.50, 129.00, 129.10, 131.87, 131.91, 136.03, 137.22, 206.59, 207.03. Anal. Calcd for $C_{16}H_{22}OS$: C,73.24; H, 8.45. Found: C, 73.24; H, 8.56.

Preparation of 8-acetyl-1-phenylthiobicyclo[4.2.0]octane (1c). To a mixture of a hexane solution of $EtAlCl_2$ (0.96M, 20 ml, 19.4 mmol) and toluene (146 ml) was added a toluene (196 ml) solution of 1-phenylthiocyclohexene (18.50 g, 97.2 mmol) and methyl vinyl ketone (9.6 ml, 117 mmol) dropwise over 15 min at -78 °C. After being warmed up to -65 °C, the reaction mixture was stirred for 2 h. Then dry ether (97 ml) and a saturated $NaHCO_3$ aqueous solution (300 ml) were successively added with vigorous stirring. The usual work-up and purification described above gave **1c** (18.45 g, 73%), and a small amount of the starting alkenyl sulfide (2.76 g, 15%) was recovered. **1c**: mp 55.5-56 °C (hexane); IR (KBr) 3049, 2929, 1701, 1583, 1475, 1439, 1360, 1201, 1184, 1161, 754, 698; ^1H NMR 1.24-2.47 (m, 10.89H), 2.22 (s, 2.67H), 2.29 (s, 0.33H), 2.47-2.64 (m, 0.11H), 2.81-2.91 (m, 0.89H), 3.23 (dd, *J*= 7.4, 4.2 Hz, 0.11H), 7.21-7.34 (m, 0.33H), 7.34-7.47 (m, 2.89H), 7.52-7.60 (m, 1.78H); ^{13}C NMR (***trans*-1c**) 20.24, 20.84, 21.13, 23.21, 28.91, 30.06, 34.61, 53.48, 55.47, 129.00, 129.25, 131.45, 137.75, 207.39. Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H,

7.74. Found: C, 73.81; H, 7.76. For the preparation of **5**, ***trans*-1c** isolated by column chromatography was used.

Preparation of (1S*, 6R*, 8R*)-1-phenylthio-8-propionylbicyclo[4.2.0]octane (*trans*-1d). To a THF (3 ml) solution of diisopropylamine (121 mg, 1.2 mmol) was added a hexane solution of butyllithium (1.6M, 0.75 ml, 1.2 mmol) at 0 °C and the reaction mixture was stirred for 15 min. After cooling to -78 °C, a THF (2 ml) solution of ***trans*-1c** (260 mg, 1 mmol) was added and the reaction mixture was gradually warmed up to 0 °C over 4 h. Iodomethane (0.25 ml, 4 mmol) was added and the mixture was further stirred for 5 h. After addition of a saturated NH_4Cl aqueous solution (10 ml), the organic materials were extracted with ether (2 × 15 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 95 : 5) to afford ***trans*-1d** (245 mg, 90%). ***trans*-1d**: mp 48-49 °C (hexane); IR (KBr) 3078, 2935, 1703, 1475, 1441, 1377, 1281, 1161, 1146, 758, 698; ^1H NMR 1.07 (t, *J*= 7.3 Hz, 3H), 1.28-1.65 (m, 8H), 1.71-1.81 (m, 1H), 2.03-2.16 (m, 2H), 2.45 (dq, *J*= 18.0, 7.3 Hz, 1H), 2.60 (dq, *J*= 18.0, 7.3 Hz, 1H), 2.84-2.90 (m, 1H), 7.37-7.46 (m, 3H), 7.53-7.61 (m, 2H); ^{13}C NMR 7.27, 20.10, 20.89, 21.17, 23.28, 28.91, 34.69, 36.01, 52.47, 55.75, 129.00, 129.23, 131.53, 137.77, 209.70. Anal. Calcd for $C_{17}H_{22}OS$: C, 74.40; H, 8.08. Found: C, 74.45; H, 8.20.

In a similar manner, (1S*, 6R*, 8R*)-8-(5-methyl-4-hexenoyl)-1-phenylthiobicyclo[4.2.0]octane (***trans*-1e**) was prepared by the reaction of lithium enolate of ***trans*-1c** and prenyl bromide. ***trans*-1e**: IR (neat) 3059, 2927, 1707, 1583, 1439, 1377, 750, 706, 696; ^1H NMR 1.27-1.61 (m, 8H), 1.64 (s, 3H), 1.69 (s, 3H), 1.71-1.80 (m, 1H), 2.02-2.15 (m, 2H), 2.22-2.33 (m, 2H), 2.44-2.54 (m, 1H), 2.54-2.63 (m, 1H), 2.82-2.90 (m, 1H), 5.09-5.14 (m, 1H), 7.36-7.45 (m, 3H), 7.53-7.58 (m, 2H); ^{13}C NMR 17.62, 20.09, 20.84, 21.15, 22.03, 23.25, 25.62, 28.89, 34.62, 42.82, 52.77, 55.73, 123.08, 128.95, 129.18, 131.50, 132.37, 137.74, 208.98. Anal. Calcd for $C_{21}H_{28}OS$: C, 76.78; H, 8.59. Found: C, 76.65; H, 8.75.

Oxidation of 8-acetyl-1-phenylthiobicyclo[4.2.0]octane (1c) with potassium peroxymonosulfate (OXONE®). To a methanol (320 ml) solution of **1c** (20.64 g, 79.3 mmol) was added potassium peroxymonosulfate (73.1 g) in water (320 ml) dropwise at 0 °C. The reaction mixture was stirred overnight at room temperature and then water (1 l) was added to the mixture. The organic materials were extracted with dichloromethane (3 × 200 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The resulting crystalline material was recrystallized from hexane-AcOEt to give **4c** (20.39 g, 88%). **4c**: mp 155-156 °C (hexane-AcOEt); IR (KBr) 3068, 2943, 1701, 1583, 1446, 1298, 1275, 1147, 1126, 721, 694; ^1H NMR 0.40-0.54 (m, 0.97H), 0.76-0.86 (m, 0.03H), 1.11-1.29 (m, 2H), 1.29-1.43 (m, 3H), 1.59-1.72 (m, 1H), 1.86 (dt, *J*= 10.7, 8.7 Hz, 1H), 2.18-2.30 (m, 2H), 2.19 (s, 0.09H), 2.22 (s, 2.91H), 3.05 (dt, *J*= 10.1, 5.5 Hz, 1H), 3.64 (dd, *J*= 10.1, 8.2 Hz, 0.03H), 3.77 (dd, *J*= 10.1, 8.2 Hz, 0.97H), 7.56-7.63 (m, 2H), 7.66-7.72 (m, 1H), 7.90-7.96 (m, 2H); ^{13}C NMR (the major isomer) 19.52, 20.26, 20.52, 23.32, 24.04, 29.63, 31.15, 47.65, 66.20, 129.25, 129.83, 134.04, 137.38, 206.49. Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89. Found: C, 65.78; H, 7.04.

In a similar manner, 1-acetyl-2-butyl-2-phenylsulfonylcyclobutane (**4b**) was prepared and isolated by silica gel column chromatography. **4b**: IR (neat) 3068, 2964, 2875, 1712, 1585, 1448, 1362, 1302, 1151, 1084, 760, 723, 692; ^1H NMR 0.80 (t, *J*= 7.2 Hz, 3H), 1.13-1.31 (m, 4H), 1.68-1.79 (m, 2H), 1.85 (dddd, *J*= 12.1, 9.8, 3.1, 0.9 Hz, 1H), 1.96 (ddt, *J*= 11.6, 9.6, 3.1 Hz, 1H), 2.15 (s, 3H), 2.33 (dq, *J*= 11.6, 9.8 Hz, 1H), 2.72 (ddd, *J*= 12.1, 10.1, 9.8 Hz, 1H), 4.01 (dt, *J*= 9.5, 0.9 Hz, 1H), 7.55-7.62 (m, 2H), 7.66-7.72 (m, 1H), 7.87-7.93 (m, 2H); ^{13}C NMR 13.45, 16.68, 22.97, 23.11, 25.84, 29.23, 29.34, 47.83, 68.99, 128.95, 129.46, 133.77, 135.93, 205.94. Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.28; H, 7.53. Found: C, 64.92; H, 7.74.

Preparation of 2-butylcyclobutenyl methyl ketone (3b). To an ethanol (12 ml) solution of potassium hydroxide (85% purity, 0.912 g, 9.27 mmol) was added an ethanol (5 ml) solution of **4b** (2.48 g, 8.43 mmol) at room temperature and the reaction mixture was stirred for 15 min. After addition of water (50 ml), the organic materials were extracted with ether (2 × 50 ml) and dried (Na_2SO_4). After removal of solvent, the residue was distilled in the presence of a few pieces of crystalline 2,6-di-*tert*-butyl-4-methylphenol (BHT) to give **3b** (1.21 g, 94%), which was added a few pieces of BHT and stored in a freezer. **3b**: bp 85-87 °C /4 mmHg; IR (neat) 2960, 2933, 2873, 1668, 1628, 1417, 1369, 1252, 1203; ^1H NMR 0.93, (t, *J*= 7.3 Hz, 3H), 1.37 (tq, *J*= 7.6, 7.3 Hz, 2H), 1.44-1.55 (m, 2H), 2.21 (s, 3H), 2.35-2.42 (m, 2H), 2.42-2.49 (m, 2H), 2.49-2.55 (m, 2H); ^{13}C NMR 13.80, 22.61, 24.97, 27.94, 28.26, 29.07, 30.53, 138.63, 162.20, 194.45.

Preparation of 7-acetylbicyclo[4.2.0]oct-6-ene (3c). With the aid of heat, the sulfone **4c** (17.54 g, 60 mmol) was dissolved in HMPA (31 ml) and immediately added to an ice-cold ethereal (300 ml) suspension of sodium hydride (55% dispersion, 5.24 g, 120 mmol) with stirring. Stirring was continued at

room temperature for ca. 30 min past the time when gas evolution ceased. After cooling to -30 °C, a phosphate buffer solution (pH 7) (200 ml) was added by portions to the reaction mixture with care. The organic materials were extracted with ether (2 × 150 ml), dried (Na_2SO_4), and concentrated under reduced pressure. After addition of a few pieces of crystalline BHT, the residue was purified by distillation to yield **3c** (7.84 g, 87%), which was added a few pieces of BHT and stored in a freezer. **3c**: bp 73-74 °C /1 mmHg; IR (neat) 2933, 2852, 1668, 1635, 1444, 1369, 1315, 1298, 1244, 1188; ^{1}H NMR 1.06-1.19 (m, 1H), 1.28-1.43 (m, 2H), 1.73-1.82 (m, 1H), 1.95-2.05 (m, 1H), 2.09-2.29 (m, 3H), 2.23 (s, 3H), 2.33-2.42 (m, 1H), 2.69 (ddd, *J*= 12.8, 3.1, 3.4 Hz, 1H), 2.81 (dd, *J*= 12.8, 1.8 Hz, 1H); ^{13}C NMR 24.53, 27.01, 27.95, 28.28, 33.01, 33.40, 38.06, 133.26, 165.49, 195.05.

Reaction of 3c with trimethylsilylmethylmagnesium chloride. To an ethereal (30 ml) suspension of copper(I) iodide (2.10 g, 11 mmol) was added an ethereal solution of trimethylsilylmethylmagnesium chloride (0.77M, 28.6 ml, 22 mmol) at -30 °C and the resulting mixture was stirred for 30 min. After cooling to -50 °C, **3c** (1.50 g, 10 mmol) in ether (20 ml) was added to the reaction mixture and stirring was continued for 30 min. A saturated $NaHCO_3$ aqueous solution (50 ml) was added and the insoluble materials were filtered off through celite. The organic materials were extracted with ether (2 × 50 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane-AcOEt (98 : 2) as an eluent to give 8-acetyl-1-(trimethylsilylmethyl)bicyclo[4.2.0]octane (**2c**) (1.88 g, 79%). **2c**: IR (neat) 2933, 2860, 1707, 1454, 1356, 1250, 1182, 862, 839; ^{1}H NMR 0.01 (s, 2.25H), 0.09 (s, 6.75H), 0.56 (d, *J*= 14.4 Hz, 0.25H), 0.93 (d, *J*= 15.3 Hz, 0.75H), 1.01-1.75 (m, 9H), 1.04 (d, *J*= 14.4 Hz, 0.25H), 1.08 (d, *J*= 15.3 Hz, 0.75H), 1.86-2.36 (m, 2H), 2.00 (s, 3H), 2.80 (dd, *J*= 9.9, 7.5 Hz, 0.75H), 3.26 (t, *J*= 8.1 Hz, 0.25H); ^{13}C NMR 0.45, 0.93, 21.09, 21.35, 21.83, 22.22, 22.47, 24.63, 24.78, 29.41, 29.82, 29.93, 30.48, 32.30, 34.37, 35.49, 36.51, 44.68, 44.72, 51.86, 54.81, 209.09, 209.75. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.62; H, 11.24.

In a similar manner, 1-acetyl-2-butyl-2-(trimethylsilylmethyl)cyclobutane (**2b**) was prepared using **3b**.

2b: IR (neat) 2968, 1707, 1468, 1358, 1250, 1178, 860, 843; ^{1}H NMR -0.02 (s, 2.7H), 0.05 (s, 6.3H), 0.66-1.05 (m, 2H), 0.85 (t, *J*= 7.2 H, 2.1H), 0.95 (t, *J*= 7.0 Hz, 0.9H), 1.08-1.41 (m, 5H), 1.49-1.79 (m, 5H), 2.04 (s, 0.9H), 2.08 (s, 2.1H), 2.16-2.30 (m, 1H), 2.96-3.03 (m, 0.7H), 3.07-3.12 (m, 0.3H); ^{13}C NMR 0.43, 0.54, 14.03, 14.13, 15.77, 16.83, 23.16, 23.19, 23.26, 26.64, 27.09, 30.59, 31.05, 31.15, 31.90, 31.96, 36.48, 41.98, 46.61, 47.68, 55.19, 57.87, 208.91, 209.53. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 69.85; H, 11.68.

Preparation of 8-propionyl-1-(trimethylsilylmethyl)bicyclo[4.2.0]octane (2d) by the methylation of 2c. To a THF (8 ml) solution of diisopropylamine (192 mg, 1.9 mmol) was added a hexane solution of butyllithium (1.6M, 1.2 ml, 1.9 mmol) at 0 °C and the reaction mixture was stirred for 10 min. After cooling to -78 °C, a THF (3 ml) solution of **2c** (375 mg, 1.57 mmol) was added and stirring was continued for 2.3 h. The reaction mixture was warmed to 0 °C and then iodomethane (0.29 ml, 4.72 mmol) was added. After stirring for 2 h, a saturated NH_4Cl aqueous solution (10 ml) was added and the organic materials were extracted with ether (2 × 20 ml). The extract was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 98 : 2) to afford **2d** (359 mg, 91%). **2d**: IR (neat) 2956, 2862, 1711, 1456, 1250, 862, 839; ^{1}H NMR -0.01 (s, 2.07H), 0.07 (s, 6.93H), 0.50 (d, *J*= 13.6 Hz, 0.23H), 0.91 (d, *J*= 15.3 Hz, 0.77H), 0.98 (t, *J*= 7.3 Hz, 2.31H), 0.99 (t, *J*= 7.3 Hz, 0.69H), 1.05 (d, *J*= 15.3 Hz, 0.77H), 1.06 (d, *J*= 13.6 Hz, 0.23H), 1.13-1.33 (m, 2H), 1.33-2.02 (m, 7H), 2.02-2.40 (m, 4H), 2.75-2.82 (m, 0.77H), 3.24 (t, *J*= 8.1 Hz, 0.23H); ^{13}C NMR 0.44, 0.91, 7.37, 7.46, 21.11, 21.39, 21.74, 22.18, 22.42, 24.62, 24.68, 24.86, 29.23, 30.06, 32.27, 34.48, 35.52, 35.66, 36.32, 36.67, 44.60, 44.76, 50.85, 53.82, 211.41, 212.06. Anal. Calcd for $C_{15}H_{28}OSi$: C, 71.36; H, 11.18. Found: C, 71.42; H, 11.39.

Addition of dimethylphenylsilyllithium to *trans*-1d and subsequent reaction with benzoyl chloride. Cerium(III) chloride (208 mg, 0.845 mmol) placed in a reaction vessel was heated (140 °C) under reduced pressure (1 mmHg) for 1 h. After cooling to 0 °C, THF (4 ml) was added and the mixture was ultrasonicated for 1 h. The reaction mixture was warmed to room temperature, and a THF (1 ml) solution of ***trans*-1d** (155 mg, 0.563 mmol) was added. After stirring for 30 min, the reaction mixture was again cooled to -78 °C and a THF solution of dimethylphenylsilyllithium (0.33M, 2.6 ml, 0.85 mmol) was added and stirring was continued for 1 h. A saturated $NaHCO_3$ aqueous solution (15 ml) was added and the insoluble materials were filtered off through celite. Organic materials were extracted with ether (2 × 20 ml), dried (Na_2SO_4), and concentrated under reduced pressure to give the crude alcohol **6d**. To a THF (3 ml) solution of **6d** was added a hexane solution of butyllithium (1.6M, 0.39 ml, 0.619 mmol) and the reaction mixture was stirred for 15 min. After a THF (1 ml) solution of benzoyl chloride (103 mg, 0.732 mmol) was added, the mixture was warmed up to room

temperature and stirring was continued for 5 h. A phosphate buffer solution (pH 7, 15 ml) was added and the organic materials were extracted with ether (2 × 20 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 95 : 5) to afford 1-(dimethylphenylsilyl)-1-(1-phenylthiobicyclo[4.2.0]octan-8-yl)propyl benzoate (**9d**) (154 mg, 53%). **9d**: mp 112-113 °C (MeOH); IR (neat) 3070, 2925, 1716, 1450, 1298, 1124, 818, 750, 737, 706; ^{1}H NMR 0.40 (s, 3H), 0.50 (s, 3H), 0.90-2.29 (m, 11H), 1.28 (t, *J*= 7.6 Hz, 3H), 2.33-2.85 (m, 3H), 7.17-7.65 (m, 13H), 8.00-8.15 (m, 2H); ^{13}C NMR -1.02, -0.52, 10.57, 21.33, 21.40, 23.40, 25.25, 28.40, 29.69, 34.76, 49.08, 57.11, 84.97, 127.34, 128.46, 128.62, 128.68, 129.45, 130.75, 132.31, 132.72, 134.74, 137.57, 137.73, 139.65, 166.80. Anal. Calcd for $C_{32}H_{38}O_2SSi$: C, 74.66; H, 7.44. Found: C, 74.35; H, 7.32.

In a similar manner, the following benzoates **9** were prepared.

1-(Dimethylphenylsilyl)-1-(2-methyl-2-phenylthiocyclobutyl)ethyl benzoate (9a): mp 73-74 °C (MeOH); IR (neat) 3070, 2964, 1705, 1450, 1371, 1298, 1109, 837, 816, 777, 739, 706; ^{1}H NMR 0.35 (s, 3H), 0.48 (s, 3H), 1.52-1.87 (m, 2H), 1.69 (s, 3H), 1.78 (s, 3H), 1.87-2.27 (m, 2H), 2.36-2.54 (m, 1H), 7.17-7.63 (m, 13H), 7.91-8.07 (m, 2H); ^{13}C NMR -3.22, -1.82, 20.10, 20.26, 23.57, 33.97, 50.93, 54.73, 80.83, 127.59, 128.29, 128.35, 128.67, 128.90, 129.28, 131.22, 132.56, 132.81, 134.12, 136.23, 138.35, 166.73. Anal. Calcd for $C_{28}H_{32}O_2SSi$: C, 73.00; H, 7.00. Found: C, 72.79; H, 6.91.

1-(Dimethylphenylsilyl)-1-(1-phenylthiobicyclo[4.2.0]octan-8-yl)ethyl benzoate (9c): mp 138-139 °C (MeOH); IR (neat) 3070, 2927, 1716, 1450, 1315, 1120, 1026, 837, 816, 750, 739, 706; ^{1}H NMR 0.35 (s, 3H), 0.49 (s, 3H), 1.21-1.81 (m, 8H), 1.86 (s, 3H), 1.92-2.22 (m, 3H), 2.68-2.88(m, 1H), 7.16-7.62 (m, 13H), 7.96-8.10 (m, 2H); ^{13}C NMR -3.32, -2.01, 21.19, 21.35, 21.63, 23.54, 24.09, 29.48, 34.84, 49.22, 56.86, 80.94, 127.63, 128.41, 128.53, 128.65, 128.90, 129.27, 131.26, 132.19, 132.56, 134.14, 137.57, 138.59, 166.32. Calcd for $C_{31}H_{36}O_2SSi$: C, 74.35; H, 7.25. Found: C, 74.27; H, 7.13.

1-(Dimethylphenylsilyl)-1-(1-phenylthiobicyclo[4.2.0]octan-8-yl)-5-methylhex-4-enyl benzoate (9e): IR (neat) 3072, 2925, 1709, 1450, 1292, 1122, 1026, 837, 818, 777, 750, 706; ^{1}H NMR 0.41 (s, 3H), 0.54 (s, 3H), 1.04-2.12 (m, 11H), 1.64 (s, 3H), 1.69 (s, 3H), 2.23-2.49 (m, 4H), 2.57-2.79 (m, 1H), 5.07-5.19 (m, 1H), 7.19-7.65 (m, 13H), 7.98-8.11 (m, 2H); ^{13}C NMR -1.19, 0.49, 18.03, 21.38, 23.48, 24.60, 25.15, 25.71, 29.62, 34.79, 35.45, 49.40, 57.19, 84.46, 124.45, 125.06, 127.42, 128.47, 128.64, 128.67, 129.44, 130.81, 131.49, 132.40, 132.72, 134.72, 137.52, 139.52, 166.72.

Ring opening reaction of 9d. To a dichloromethane solution of titanium(IV) isopropoxide (0.73M, 0.15 ml, 0.11 mmol) diluted with dichloromethane (2 ml) was added a dichloromethane solution of titanium(IV) chloride (1.03M, 0.33 ml, 0.34 mmol) at 0 °C, and the mixture was stirred for 10 min. Then the mixture was cooled to -78 °C and a dichloromethane solution of trimethylphenylthiosilane (1.01M, 0.45 ml, 0.45 mmol) was added. After stirring for 10 min, a dichloromethane (2 ml) solution of benzoate **9d** (154 mg, 0.299 mmol) was added and stirring was continued for 7.5 h. The reaction mixture was warmed to -30 °C and stirred for additional 20.5 h. A saturated $NaHCO_3$ aqueous solution (15 ml) was added and the insoluble materials were filtered off through celite. Organic materials were extracted with dichloromethane (2 × 15 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 98 : 2) to afford (*E*)-1-[3-(dimethylphenylsilyl)pent-2-enyl]-2,2-bis(phenylthio)cyclohexane (***E*-8d**) (96 mg, 64%). ***E*-8d**: IR (neat) 3068, 2933, 1610, 1583, 1439, 1254, 1111, 831, 812, 750, 733, 702, 692; ^{1}H NMR 0.37 (s, 6H), 0.81-1.07 (m, 1H), 0.92 (t, *J*= 7.6 Hz, 3H), 1.22-1.93 (m, 8H), 2.13-2.35 (m, 3H), 3.36 (dd, *J*= 4.8, 15.0 Hz, 1H), 5.68 (dd, *J*= 5.0, 8.2 Hz, 1H), 7.18-7.46 (m, 11H), 7.49-7.60 (m, 2H), 7.70-7.86 (m, 2H); ^{13}C NMR -2.52, 14.65, 22.96, 23.08, 25.65, 28.05, 30.33, 36.46, 45.72, 71.23, 127.60, 128.44, 128.48, 128.69, 128.90, 129.04, 130.38, 131.79, 134.00, 137.21, 137.65, 139.25 140.77, 142.07. Anal. Calcd for $C_{31}H_{38}S_2Si$: C, 74.05; H, 7.62. Found: C, 74.22; H, 7.78.

In a similar manner, the following thioacetals **8** were obtained.

***(E)*-2-(Dimethylphenylsilyl)-6,6-bis(phenylthio)hept-2-ene (*E*-8a):** IR (neat) 3068, 2958, 1618, 1583, 1439, 1248, 1111, 831, 814, 750, 701, 692; ^{1}H NMR 0.31 (s, 6H), 1.39 (s, 3H), 1.68 (s, 3H), 1.74-1.84 (m, 2H), 2.39-2.57 (m, 2H), 5.63-5.75 (m, 1H), 7.23-7.42 (m, 9H), 7.42-7.53 (m, 2H), 7.59-7.70 (m, 4H); ^{13}C NMR -3.44, 14.88, 24.38, 28.17, 40.81, 64.05, 127.67, 128.54, 128.79, 129.01, 132.02, 133.93, 134.91, 136.90, 138.62, 140.11. Calcd for $C_{27}H_{32}S_2Si$: C, 72.27; H, 7.18. Found: C, 72.17; H, 7.20.

***(E)*-1-[3-(Dimethylphenylsilyl)but-2-enyl]-2,2-bis(phenylthio)cyclohexane (*E*-8c):** IR (neat) 3068, 2935, 1618, 1583, 1439, 1248, 1111, 833, 814, 773, 750, 731, 702, 692; ^{1}H NMR 0.35 (s, 3H), 0.36 (s, 3H), 0.87-1.01 (m, 1H), 1.24-1.54 (m, 2H), 1.54-1.71 (m, 4H), 1.77 (s, 3H), 1.71-1.85 (m, 2H), 2.17-2.29 (m, 1H), 3.34 (dd, *J*= 14.7, 5.0 Hz, 1H), 5.71-5.77 (m, 1H), 7.20-7.27 (m, 2H), 7.29-7.39 (m, 7H), 7.39-7.43 (m, 2H), 7.48-7.55 (m, 2H), 7.75-7.81 (m, 2H); ^{13}C NMR -3.29, 15.33, 22.98, 25.66, 28.02, 30.60, 36.46, 45.75, 71.30, 127.69, 128.45, 128.49, 128.77, 128.91, 129.05, 130.42, 131.87,

133.97, 135.50, 137.24, 137.67, 138.79, 140.36. Anal. Calcd for $C_{30}H_{36}S_2Si$: C, 73.71; H, 7.42. Found: C, 73.64; H, 7.50.

(*E* and *Z*)-1-[3-(Dimethylphenylsilyl)-7-methylocta-2,6-dienyl]-2,2-bis(phenylthio)-cyclohexane (8e): IR (neat) 3068, 2933, 1608, 1583, 1439, 1248, 1111, 829, 812, 750, 702, 692; ^{1}H NMR 0.38 (s, 5.4H), 0.49 (s, 0.3H), 0.50 (s, 0.3H), 0.82-1.00 (m, 1H), 1.22-1.46 (m, 2H), 1.46-1.85 (m, 5.3H), 1.51 (s, 0.3H), 1.56 (s, 2.7H), 1.66 (s, 2.7H), 1.87-2.05 (m, 2H), 2.09-2.33 (m, 4H), 3.28 (d, *J*= 14.5 Hz, 0.1H), 3.36 (dd, *J*= 14.7, 4.8 Hz, 0.9H), 5.04-5.09 (m, 0.1H), 5.09-5.16 (m, 0.9H), 5.72 (dd, *J*= 8.1, 4.8 Hz, 0.9H), 5.91 (dd, *J*= 9.2, 4.0 Hz, 0.1H), 7.20-7.43 (m, 11H), 7.50-7.56 (m, 1.8H), 7.58-7.60 (m, 0.2H), 7.71-7.74 (m, 0.2H), 7.76-7.81 (m, 1.8H); ^{13}C NMR (the major isomer) -2.49, 17.64, 22.98, 25.68, 25.72, 28.10, 28.65, 30.47, 30.69, 36.49, 45.77, 71.22, 124.52, 127.64, 128.45, 128.50, 128.73, 128.91, 129.05, 130.47, 131.46, 131.86, 134.02, 137.25, 137.68, 139.22, 140.29, 141.60, 143.57. Anal. Calcd for $C_{35}H_{44}S_2Si$: C, 75.48; H, 7.96. Found: C, 75.47; H, 8.01.

Hydrolysis of *E*-8d. To an acetonitrile (8 ml)-water (1 ml) suspension of mercury(II) chloride (207 mg, 0.762 mmol) was added an acetonitrile (4 ml) solution of ***E*-8d** (96 mg, 0.191 mmol) at room temperature. After stirring for 2 h, brine (30 ml) was added and the insoluble materials were filtered off through celite. The organic materials were extracted with pentane (2 × 20 ml), washed with a saturated $NaHCO_3$ aqueous solution and brine, and dried (Na_2SO_4). After removing the solvent, the residue was purified by PTLC (hexane-AcOEt, 9 : 1) to afford (*E*)-2-[3-(dimethylphenylsilyl)pent-2-enyl]cyclohexanone (***E*-5d**) (53 mg, 92%). ***E*-5d**: IR (neat) 3068, 2935, 1716, 1612, 1429, 1248, 1111, 831, 812, 771, 731, 702; ^{1}H NMR 0.33 (s, 6H), 0.83 (t, *J*= 7.7 Hz, 3H), 1.22-1.45 (m, 1H), 1.52-1.94 (m, 3H), 1.94-2.24 (m, 5H), 2.24-2.49 (m, 3H), 2.49-2.65 (m, 1H), 5.65-5.81 (m, 1H), 7.28-7.39 (m, 3H), 7.43-7.55 (m, 2H); ^{13}C NMR -2.64, 14.62, 22.73, 25.06, 27.93, 28.07, 33.52, 42.04, 50.70, 127.58, 128.69, 133.96, 139.14, 139.20, 142.35, 212.62. Anal. Calcd for $C_{19}H_{28}OSi$: C, 75.94; H, 9.39. Found: C, 75.80; H, 9.60.

In a similar manner, the following alkenylsilanes **5** were obtained.

(*E*)-6-(Dimethylphenylsilyl)hept-5-en-2-one (*E*-5a): IR (neat) 3070, 2960, 1718, 1618, 1429, 1363, 1248, 1111, 833, 814, 775, 733, 702; ^{1}H NMR 0.32 (s, 6H), 1.67 (s, 3H), 2.12 (s, 3H), 2.14-2.56 (m, 4H), 5.73 (qt, *J*= 6.3, 1.7 Hz, 1H), 7.29-7.38 (m, 3H), 7.41-7.54 (m, 2H); ^{13}C NMR -3.53, 14.70, 22.93, 29.86, 43.05, 127.65, 128.80, 133.89, 135.69, 138.41, 139.19, 208.29. Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 8.99. Found: C, 72.99; H, 8.89.

(*E*)-2-[3-(Dimethylphenylsilyl)but-2-enyl]cyclohexanone (*E*-5c): IR (neat) 3068, 2937, 1714, 1618, 1429, 1248, 1126, 1111, 833, 816, 773, 731, 702; ^{1}H NMR 0.32 (s, 6H), 1.25-1.44 (m, 1H), 1.55-1.76 (m, 2H), 1.66 (s, 3H), 1.77-1.91 (m, 1H), 1.97-2.22 (m, 3H), 2.22-2.45 (m, 3H), 2.49-2.61 (m, 1H), 5.70-5.84 (m, 1H), 7.28-7.38 (m, 3H), 7.44-7.53 (m, 2H); ^{13}C NMR -3.48, 14.86, 24.97, 27.88, 28.21, 33.42, 41.96, 50.49, 127.58, 128.69, 133.83, 135.71, 138.53, 138.79, 212.59. Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.32; H, 9.25.

(*E* and *Z*)-2-[3-(Dimethylphenylsilyl)-7-methylocta-2,6-dienyl]cyclohexanone (5e): IR (neat) 3068, 2935, 2860, 1714, 1429, 1248, 1111, 831, 812, 773, 731, 702; ^{1}H NMR 0.34 (s, 5.4H), 0.39 (s, 0.3H), 0.40 (s, 0.3H), 1.23-1.73 (m, 3H), 1.49 (s, 2.7H), 1.56 (s, 0.3H), 1.63 (s, 2.7H), 1.67 (s, 0.3H), 1.73-1.95 (m, 3H), 1.95-2.50 (m, 8H), 2.50-2.66 (m, 1H), 4.97-5.14 (m, 1H), 5.69-5.83 (m, 0.9H), 5.98-6.09 (m, 0.1H), 7.28-7.39 (m, 3H), 7.44-7.56 (m, 2H); ^{13}C NMR -2.58, -1.09, -0.93, 17.55, 17.74, 24.97, 25.08, 25.64, 25.69, 27.88, 27.93, 28.35, 28.66, 29.56, 30.12, 31.77, 33.31, 33.57, 38.41, 41.94, 42.05, 50.75, 51.09, 124.36, 124.43, 127.62, 127.69, 128.67, 128.73, 131.27, 131.35, 133.86, 133.98, 138.70, 139.10, 139.92, 139.96, 140.54, 142.20, 212.42, 212.49. Anal. Calcd for $C_{23}H_{34}OSi$: C, 77.90; H, 9.66. Found: C, 77.64; H, 9.90.

Addition of dimethylphenylsilyllithium to 2d and subsequent ring opening reaction. Cerium(III) chloride (111 mg, 0.45 mmol) placed in a reaction vessel was heated (140 °C) under reduced pressure (1 mmHg) for 1 h. After cooling to 0 °C, THF (2 ml) was added and the mixture was ultrasonicated for 1 h. The reaction mixture was warmed to room temperature and a THF (1 ml) solution of **2d** (76 mg, 0.3 mmol) was added. After stirring for 30 min, the reaction mixture was again cooled to -78 °C, and a THF solution of dimethylphenylsilyllithium (0.33M, 1.36 ml, 0.45 mmol) was added. After 1 h, a saturated $NaHCO_3$ aqueous solution (15 ml) was added, and the insoluble materials were filtered off through celite. Organic materials were extracted with ether (2 × 20 ml), dried (Na_2SO_4), and concentrated under reduced pressure to give the crude alcohol **18d**. To a dichloromethane (2 ml) suspension of zinc bromide (74 mg, 0.33 mmol) was added a dichloromethane (2 ml) solution of crude **18d** at room temperature with stirring. After 3 h, a saturated $NaHCO_3$ aqueous solution (10 ml) was added, and the insoluble materials were filtered off through celite. Organic materials were extracted with dichloromethane (2 × 15 ml), dried (Na_2SO_4), and concentrated under reduced pressure.

The residue was purified by PTLC (hexane) to afford (*E*)-2-methylidene-1-[3-(dimethylphenylsilyl)pent-2-enyl]cyclohexane (***E*-19d**) (48 mg, 53%). ***E*-19d**: IR (neat) 3070, 2933, 2856, 1645, 1612, 1427, 1248, 1111, 889, 831, 812, 771, 729, 700; ^{1}H NMR 0.34 (s, 6H), 0.85 (t, *J*= 7.6 Hz, 3H), 1.07-1.30 (m, 1H), 1.30-1.86 (m, 5H), 1.92-2.48 (m, 7H), 4.58 (s, 1H), 4.67 (s, 1H), 5.80 (t, *J*= 6.1 Hz, 1H), 7.27-7.41 (m, 3H), 7.44-7.61 (m, 2H); ^{13}C NMR -2.58, -2.56, 14.58, 22.88, 24.80, 28.72, 31.23, 33.71, 35.31, 43.23, 105.54, 127.56, 128.64, 134.01, 139.40, 140.97, 141.04, 152.66. Anal. Calcd for $C_{20}H_{30}Si$: C, 80.46; H, 10.13. Found: C, 80.37; H, 10.36.

In a similar manner, alkenylsilanes **19b** and **c** were obtained. Alkenylgermanes **20b-d** were also obtained using a THF solution of triethylgermyllithium (1.5 equiv), prepared from triethylgermane and *tert*-butyllithium in the presence of tetramethylethylenediamine.[17]

(*E*)-2-Butyl-6-(dimethylphenylsilyl)hepta-1,5-diene (*E*-19b): IR (neat) 3068, 2956, 2927, 1645, 1618, 1429, 1248, 1111, 831, 814, 773, 729, 700; ^{1}H NMR 0.32 (s, 6H), 0.91 (t, *J*= 7.1 Hz, 3H), 1.20-1.51 (m, 4H), 1.66 (s, 3H), 1.95-2.14 (m, 4H), 2.18-2.34 (m, 2H), 4.72 (s, 2H), 5.81 (tq, *J*= 6.5, 1.7 Hz, 1H), 7.29-7.38 (m, 3H), 7.42-7.58 (m, 2H); ^{13}C NMR -3.42, 14.01, 14.75, 22.49, 26.97, 30.03, 35.44, 35.85, 108.78, 127.64, 128.74, 133.96, 134.09, 138.78, 141.23, 149.71. Anal. Calcd for $C_{19}H_{30}Si$: C, 79.65; H, 10.55. Found: C, 79.82; H, 10.65.

(*E*)-1-[3-(Dimethylphenylsilyl)but-2-enyl]-2-methylidenecyclohexane (*E*-19c): IR (neat) 3068, 2956, 2856, 1645, 1618, 1429, 1248, 1111, 887, 833, 816, 773, 729, 700; ^{1}H NMR 0.32 (s, 6H), 1.07-1.31 (m, 1H), 1.31-1.52 (m, 2H), 1.52-1.87 (m, 3H), 1.66 (s, 3H), 1.94-2.45 (m, 5H), 4.57 (s, 1H), 4.66 (s, 1H), 5.84 (tq, *J*= 7.1, 1.7 Hz, 1H), 7.27-7.42 (m, 3H), 7.42-7.58 (m, 2H); ^{13}C NMR -3.38, -3.35, 14.97, 24.87, 28.73, 31.51, 33.69, 35.38, 43.01, 105.42, 127.63, 128.71, 133.95, 134.39, 138.87, 140.69, 152.74. Anal. Calcd for $C_{19}H_{28}Si$: C, 80.21; H, 9.92. Found: C, 80.15; H, 10.03.

(*E*)-2-Butyl-6-(triethylgermyl)hepta-1,5-diene (*E*-20b): IR (neat) 3072, 2964, 2873, 1645, 1622, 1458, 1022, 889, 706; ^{1}H NMR 0.64-0.83 (m, 6H), 0.83-1.09 (m, 12H), 1.16-1.49 (m, 4H), 1.69 (s, 3H), 1.91-2.13 (m, 4H), 2.13-2.28 (m, 2H), 4.67 (s, 2H), 5.49 (tq, *J*= 6.6, 1.7 Hz, 1H); ^{13}C NMR 3.49, 8.92, 13.98, 16.32, 22.50, 26.57, 30.07, 35.81, 35.85, 108.71, 134.77, 137.91, 149.82. Anal. Calcd for $C_{17}H_{34}Ge$: C, 65.65; H, 11.02. Found: C, 65.33; H, 10.96.

(*E*)-1-Methylidene-2-[3-(triethylgermyl)but-2-enyl]cyclohexane (*E*-20c): IR (neat) 3084, 2958, 2873, 1645, 1624, 1446, 1022, 887, 706; ^{1}H NMR 0.67-0.87 (m, 6H), 0.92-1.10 (m, 9H), 1.10-1.28 (m, 1H), 1.28-1.55 (m, 2H), 1.55-1.86 (m, 3H), 1.72 (s, 3H), 1.94-2.41 (m, 5H), 4.57 (s, 1H), 4.65 (s, 1H), 5.46-5.58 (m, 1H); ^{13}C NMR 3.43, 8.95, 16.53, 24.89, 28.78, 31.12, 33.59, 35.40, 43.19, 105.32, 135.06, 137.27, 152.91. Anal. Calcd for $C_{17}H_{32}Ge$: C, 66.07; H, 10.44. Found: C, 66.14; H, 10.48.

(*E*)-1-Methylidene-2-[3-(triethylgermyl)pent-2-enyl]cyclohexane (*E*-20d): IR (neat) 3082, 2962, 2873, 1645, 1616, 1446, 1020, 887, 706; ^{1}H NMR 0.69-0.87 (m, 6H), 0.93 (t, *J*= 8.3 Hz, 3H), 0.89-1.08 (m, 9H), 1.10-1.29 (m, 1H), 1.29-1.85 (m, 5H), 1.94-2.42 (m, 7H), 4.58 (s, 1H), 4.66 (s, 1H), 5.42-5.55 (m, 1H); ^{13}C NMR 4.16, 8.93, 14.35, 24.08, 24.82, 28.78, 30.88, 33.62, 35.34, 43.43, 105.44, 137.24, 141.68, 152.82. Anal. Calcd for $C_{18}H_{34}Ge$: C, 66.92; H, 10.61. Found: C, 67.20; H, 10.84.

Preparation of Authentic alkenylsilanes and germanes utilizing acylsilanes and germanes

The results of preparation of authentic alkenylsilanes **5** and **19** and alkenylgermanes **20** and **28** (Scheme 9 and 14) were summarized in Table 7. The starting materials, acylsilanes **12** and **13** and acylgermanes **22** and **23**, were prepared according to the methods reported by Soderquist [21] and Reich.[22]

Preparation of acetyldimethylphenylsilane (12). To a THF(15 ml) solution of methyl vinyl ether (19.2 mmol) was added a pentane solution of *tert*-butyllithium (1.5M, 8 ml, 12 mmol) at -65 °C with stirring and the reaction mixture was warmed to 0 °C over 15 min. The reaction mixture was cooled again to -65 °C and chlorodimethylphenylsilane (1.68 ml, 10 mmol) was added. The mixture was gradually warmed up to room temperature over 14 h and then a saturated NH_4Cl aqueous solution (30 ml) was added. The organic materials were extracted with ether (2 × 40 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was dissolved in a 0.2M HCl acetone-water (4 : 1) solution (20 ml) and the mixture was stirred for 1 h. It was diluted with water (40 ml) and the organic materials were extracted with ether (2 × 30 ml). The extract was dried (Na_2SO_4) and concentrated under reduced pressure. Purification was achieved by distillation to afford **12** (1.587 g, 89%). **12**: bp 71-72 °C / 0.8 mmHg; IR (neat) 3072, 2966, 1647, 1429, 1252, 1111, 839, 816, 783, 737, 704; ^{1}H NMR 0.49 (s, 6H), 2.23 (s, 3H), 7.34-7.45 (m, 3H), 7.52-7.58 (m, 2H); ^{13}C NMR -4.94, 35.87, 128.14, 129.89, 133.89, 134.24, 245.27. Anal. Calcd for $C_{10}H_{14}OSi$: C, 67.36; H, 7.91. Found: C, 67.02; H, 8.08.

Table 7. Preparation of Authentic Vinylsilanes **5** and **19** and Vinylgermanes **20** and **28**.

Entry	Unsaturated ester	Allylic alcohol (Yield/%)	γ,δ-Unsaturated ketone **5** or **28**		1,5-Diene **19** or **20**	
			Source of lithium enolate	Product (Yield/%)	Product (Yield/%)	
1	***E*-14**	***E*-16** (81)	2-(Trimethylsiloxy)propene	***E*-5a** (7)		
2			2-Hexanone	***E*-5b** (16)	***E*-19b**	(82)
3			Cyclohexanone	***E*-5c** (48)	***E*-19c**	(86)
4	***Z*-14**	***Z*-16** (89)	2-(Trimethylsiloxy)propene	***Z*-5a** (3)		
5			2- Hexanone	***Z*-5b** (7)	***Z*-19b**	(91)
6			Cyclohexanone	***Z*-5c** (21)	***Z*-19c**	(87)
7	***E*-15**	***E*-17** (86)	Cyclohexanone	***E*-5d** (14)	***E*-19d**	(78)
8	***Z*-15**	***Z*-17** (93)	Cyclohexanone	***Z*-5d** (13)	***Z*-19d**	(79)
9	***E*-24**	***E*-26** (89)	2-Hexanone	***E*-28b** (24)	***E*-20b**	(66)
10			Cyclohexanone	***E*-28c** (49)	***E*-20c**	(68)
11	***Z*-24**	***Z*-26** (87)	2-Hexanone	***Z*-28b** (6)	***Z*-20b**	(78)
12			Cyclohexanone	***Z*-28c** (13)	***Z*-20c**	(68)
13	***E*-25**	***E*-27** (87)	Cyclohexanone	***E*-28d** (17)	***E*-20d**	(81)
14	***Z*-25**	***Z*-27** (87)	Cyclohexanone	***Z*-28d** (6)	***Z*-20d**	(76)

In a similar manner, acetyltriethylgermane (**22**) was prepared using triethylgermylchloride in 70% yield. **22**: bp 76-79 °C /15 mmHg (lit.[23] bp 65 °C / 8 mmHg); IR (neat) 2968, 2877, 1662, 1464, 1429, 1340, 1119, 1024, 706; ^{1}H NMR 0.92-1.00 (m, 6H), 1.04-1.10 (m, 9H), 2.29 (s, 3H); ^{13}C NMR 3.90, 8.90, 38.46, 245.14. Anal. Calcd for $C_8H_{18}GeO$: C, 47.38; H, 8.95. Found: C, 47.21; H, 9.12.

Preparation of dimethylphenyl(propionyl)silane (13). To a THF (16 ml) solution of 2-ethyl-1,3-dithiane (1.19 g, 8 mmol) was added a hexane solution of butyllithium (1.6 M, 5.3 ml, 8.4 mmol) at -40 °C and the reaction mixture was warmed to 0 °C. After stirring for 1.7 h, chlorodimethylphenylsilane (1.50 ml, 8.8 mmol) was added and stirring was continued for 2 h. A saturated $NaHCO_3$ aqueous solution (20 ml) was added and the organic materials were extracted with ether (2 × 20 ml). The ethereal extract was dried (Na_2SO_4) and concentrated under reduced pressure. To a methanol-water (4 : 1, 24 ml) solution of the residue was added chloramin T trihydrate (9.11 g, 40 mmol) at 0 °C. After 30 min, the mixture was warmed to room temperature and stirring was continued for additional 10 min. A saturated $NaHCO_3$ aqueous solution (30 ml) was added, and the organic materials were extracted with ether (2 × 20 ml) and dried (Na_2SO_4). After removal of solvent under reduced pressure, the residue was purified by column chromatography (hexane-AcOEt, 98 : 2) to afford **13** (1.24 g, 80%). **13**: IR (neat) 3072, 2971, 2937, 1645, 1429, 1250, 1111, 837, 818, 783, 735, 700; ^{1}H NMR 0.49 (s, 6H), 0.91 (t, *J*= 7.2 Hz, 3H), 2.59 (q, *J*= 7.2 Hz, 2H), 7.32-7.45 (m, 3H), 7.50-7.61 (m, 2H); ^{13}C NMR -4.78, 6.07, 41.87, 128.09, 129.79, 133.90, 134.59, 246.11. Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.38. Found: C, 68.32; H, 8.41.

In a similar manner, triethyl(propionyl)germane (**23**) was prepared in 53% yield. **23**: IR (neat) 2954, 2873, 1658, 1460, 1425, 1022, 706; ^{1}H NMR 0.87-1.19 (m, 18H), 2.61 (q, *J*=7.3 Hz, 2H); ^{13}C NMR 3.99, 6.01, 8.94, 44.65, 245.81. Anal. Calcd for $C_9H_{20}GeO$: C, 49.85; H, 9.30. Found: C, 49.52; H, 9.37.

Preparation of ethyl (*E*)-3-(triethylgermyl)-2-butenoate (*E*-24). To a mineral oil dispersion of sodium hydride (55%, 87 mg, 2 mmol) was added a benzene (2 ml) solution of triethyl phosphonoacetate (448 mg, 2 mmol) at room temperature with stirring. After 1 h, **22** (406 mg, 2 mmol) was added dropwise and the reaction mixture was heated at 60~65 °C for 30 min. After cooling the mixture was diluted with hexane (30 ml) and the resulting insoluble materials were separated by decantation. The hexane solution was concentrated under reduced pressure and the residue was purified by PTLC (hexane-AcOEt, 98 : 2) to afford ***E*-24** (418 mg, 77%) and ***Z*-24** (15 mg, 3%). ***E*-24:** IR (neat) 2956, 2873, 1716, 1610, 1464, 1338, 1188, 1039, 1022, 706; ^{1}H

NMR 0.79-0.96 (m, 6H), 0.96-1.11 (m, 9H), 1.30 (t, *J*= 7.1 Hz, 3H), 2.29 (d, *J*= 1.7 Hz, 3H), 4.16 (q, *J*= 7.1 Hz, 2H), 5.94 (q, *J*= 1.7 Hz, 1H); ^{13}C NMR 3.41, 8.74, 14.29, 19.28, 59.50, 125.89, 163.93, 165.04. Anal. Calcd for $C_{12}H_{24}GeO_2$: C, 52.81; H, 8.86. Found: C, 52.67; H, 8.92. **Z-24**: IR (neat) 2949, 2872, 1716, 1608, 1439, 1367, 1325, 1192, 1045, 1012, 866, 708; ^{1}H NMR 0.95-1.04 (m, 15H), 1.28 (t, *J*= 7.1 Hz, 3H), 2.03 (d, *J*= 1.7 Hz, 1H), 4.17 (q, *J*= 7.1 Hz, 2H), 6.37 (q, *J*= 1.7 Hz, 1H); ^{13}C NMR 4.84, 9.11, 14.30, 27.14, 59.77, 129.32, 164.03, 166.52. Anal. Calcd for $C_{12}H_{24}GeO_2$: C, 52.81; H, 8.86. Found: C, 53.13; H, 9.07.

Preparation of ethyl (*Z*)-3-dimethylphenylsilyl-2-butenoate (*Z*-14). To a THF (3 ml) solution of 1,1,1,3,3,3-hexamethyldisilazane (194 mg, 1.2 mmol) was added a hexane solution of butyllithium (1.6M, 0.75 ml, 1.2 mmol) at 0 °C and the reaction mixture was stirred for 20 min. After cooling to -78°C, ethyl (trimethylsilyl)acetate (192 mg, 1.2 mmol) in THF (1 ml) was added, and stirring was continued for 15 min. A THF (1 ml) solution of **12** (178 mg, 1 mmol) was added, and the reaction mixture was stirred at the same temperature for 1 h. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. A saturated NH_4Cl aqueous solution (10 ml) was added, and the organic materials were extracted with ether (2 × 15 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 98 : 2) to afford ***E*-14** (34 mg, 14%) and ***Z*-14** (168 mg, 68%). ***E*-14**: IR (neat) 3072, 2962, 1716, 1612, 1429, 1338, 1252, 1188, 1115, 837, 818, 779, 737, 702; ^{1}H NMR 0.38 (s, 6H), 1.25 (t, *J*= 7.1 Hz, 3H), 2.16 (d, *J*= 1.7 Hz, 3H), 4.15 (q, *J*= 7.1 Hz, 2H), 6.06 (q, *J*= 1.7 Hz, 1H), 7.29-7.38 (m, 3H), 7.42-7.51 (m, 2H); ^{13}C NMR -4.02, 14.25, 17.41, 59.65, 127.78, 127.90, 129.39, 133.94, 136.12, 159.76, 165.57. Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.41; H, 8.15. ***Z*-14**: IR (neat) 3072, 2960, 1724, 1606, 1429, 1333, 1248, 1205, 1113, 874, 841, 820, 781, 739, 704; ^{1}H NMR 0.48 (s, 6H), 1.13 (t, *J*= 7.1 Hz, 3H), 1.94 (d, *J*= 1.7 Hz, 3H), 4.01 (q, *J*= 7.1 Hz, 2H), 6.42 (q, *J*= 1.7 Hz, 1H), 7.27-7.35 (m, 3H), 7.47-7.58 (m, 2H); ^{13}C NMR -2.02, 14.06, 26.78, 59.90, 127.52, 128.60, 131.98, 133.62, 138.73, 159.18, 166.31. Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.66; H, 8.21

In a similar manner, both stereoisomers of the following unsaturated esters **15** and **25** were prepared.

Ethyl (*E*)-3-(dimethylphenylsilyl)pent-2-enoate (*E*-15): IR (neat) 3072, 2979, 1722, 1604, 1252, 1184, 835, 817, 777, 735, 702; ^{1}H NMR 0.43 (s, 6H), 0.95 (t, *J*= 7.6 Hz, 3H), 1.28 (t, *J*= 7.1 Hz, 3H), 2.66 (q, *J*= 7.6 Hz, 2H), 4.16 (q, *J*= 7.1 Hz, 2H), 6.06 (s, 1H), 7.29-7.41 (m, 3H), 7.45-7.55 (m, 2H); ^{13}C NMR -3.35, 14.16, 14.22, 24.51, 59.69, 127.72, 127.87, 129.35, 134.00, 136.59, 165.20, 165.72. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.52; H, 8.68.

Z-15: IR (neat) 3070, 2968, 1718, 1603, 1248, 1200, 838, 818, 779, 737, 704; ^{1}H NMR 0.48 (s, 6H), 1.01 (t, *J*= 7.4 Hz, 3H), 1.13 (t, *J*= 7.1 Hz, 3H), 2.26 (dq, *J*= 7.4, 1.7 Hz, 2H), 3.99 (q, *J*= 7.1 Hz, 2H), 6.38 (t, *J*= 1.7 Hz, 1H), 7.23-7.35 (m, 3H), 7.47-7.59 (m, 2H); ^{13}C NMR -1.68, 13.61, 14.05, 31.95, 59.94, 127.46, 128.52, 130.34, 133.67, 139.00, 164.49, 166.73. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.70; H, 8.70.

Ethyl (*E*)-3-(triethylgermyl)pent-2-enoate (*E*-25): IR (neat) 2960, 2875, 1718, 1605, 1464, 1180, 1039, 872, 706; ^{1}H NMR 0.78-0.97 (m, 6H), 0.97-1.12 (m, 12H), 1.30 (t, *J*= 7.2 Hz, 3H), 2.74 (dq, *J*= 7.6, 1.0 Hz, 2H), 4.16 (q, *J*=7.2 Hz, 2H), 5.89 (s, 1H); ^{13}C NMR 3.97, 8.74, 13.61, 14.25, 25.95, 59.52, 125.52, 164.63, 169.66. Anal. Calcd for $C_{13}H_{26}GeO_2$: C, 54.42; H, 9.13. Found: C, 54.14; H, 9.30.

Z-25: IR (neat) 2972, 2873, 1724, 1606, 1464, 1200, 1043, 879, 708; ^{1}H NMR 0.97-1.02 (m, 15H), 1.04 (t, *J*= 7.3 Hz, 3H), 1.29 (t, *J*= 7.1 Hz, 3H), 2.31 (dq, *J*= 7.3, 1.5 Hz, 2H), 4.16 (q, *J*= 7.1 Hz, 2H), 6.31 (t, *J*= 1.5 Hz, 1H); ^{13}C NMR 4.98, 9.20, 13.50, 14.29, 32.17, 59.78, 127.55, 166.85, 169.42. Anal. Calcd for $C_{13}H_{26}GeO_2$: C, 54.42; H, 9.13. Found: C, 54.19; H, 9.30.

Preparation of (*Z*)-3-(dimethylphenylsilyl)but-2-en-1-ol (*Z*-16). To a toluene solution of diisobutylaluminum hydride (1M, 1.5 ml, 1.5 mmol) diluted with dichloromethane (1.3 ml) was added a dichloromethane (2 ml) solution of ***Z*-24** (165 mg, 0.67 mmol), and the reaction mixture was stirred for 1.5 h. After addition of a saturated $NaHCO_3$ aqueous solution, the resulting insoluble materials were filtered off through celite. The organic materials were extracted with dichloromethane (2 × 20 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 4 : 1) to afford ***Z*-16** (122 mg, 89%). **Z-16**: IR (neat) 3327, 3070, 2954, 1622, 1429, 1250, 1111, 999, 837, 816, 775, 731, 702; ^{1}H NMR 0.40 (s, 6H), 1.24 (br s, 1H), 1.88 (s, 3H), 3.96 (d, *J*= 7.0 Hz, 2H), 6.26 (tq, *J*= 7.0, 1.7 Hz, 1H), 7.29-7.40 (m, 3H), 7.45-7.57 (m, 2H); ^{13}C NMR -1.44, 24.97, 62.01, 127.96, 129.08, 133.50, 137.73, 138.97, 141.79.

In a similar manner, the following γ-silyl and γ-germyl allylic alcohols **16**, **17**, **26**, and **27** were obtained.

***E*-16:** IR (neat) 3421, 3072, 2964, 1622, 1429, 1250, 1111, 833, 818, 775, 733, 702; ^{1}H NMR 0.35 (s, 6H), 1.66-1.70 (m, 3H), 1.72-1.78 (br s, 1H), 4.26 (dd, *J*= 5.8, 0.8 Hz, 2H), 5.95 (tq, *J*= 5.8, 1.7 Hz, 1H), 7.29-7.37 (m, 3H), 7.46-7.52 (m, 2H); ^{13}C NMR -3.73, 14.95, 59.63, 127.71, 128.95, 133.89, 137.26, 137.79, 139.73.

(*E*)-3-(Dimethylphenylsilyl)pent-2-en-1-ol (*E*-17): IR (neat) 3323, 3070, 2964, 1616, 1429, 1248, 1111, 1028, 912, 833, 814, 773, 733, 702; ^{1}H NMR 0.38 (s, 6H), 0.84 (t, *J*= 7.6 Hz, 3H), 1.47-1.56 (br s, 1H), 2.16 (q, *J*= 7.6 Hz, 2H), 4.28 (d, *J*= 6.1 Hz, 2H), 5.93 (t, *J*= 6.1 Hz, 1H), 7.31-7.38 (m, 3H), 7.48-7.54 (m, 2H); ^{13}C NMR -2.97, 15.00, 23.01, 59.48, 127.69, 128.93, 133.96, 138.22, 139.97, 143.92.

***Z*-17:** IR (neat) 3464, 2968, 1653, 1429, 1252, 1111, 1014, 837, 816, 775, 731, 702; ^{1}H NMR 0.41 (s, 6H), 1.03 (t, *J*= 7.4 Hz, 3H), 1.04-1.10 (br s, 1H), 2.20 (br q, *J*= 7.4 Hz, 2H), 3.98 (d, *J*= 6.9 Hz, 2H), 6.23 (tt, *J*= 6.9, 1.4 Hz, 1H), 7.31-7.38 (m, 3H), 7.48-7.55 (m, 2H); ^{13}C NMR -1.09, 14.66, 30.74, 62.15, 127.90, 128.98, 133.51, 139.38, 140.53, 143.46.

(*E*)-3-(Triethylgermyl)but-2-en-1-ol (*E*-26): IR (neat) 3309, 2949, 2872, 1462, 1065, 1014, 706; ^{1}H NMR 0.71-0.89 (m, 6H), 0.95-1.10 (m, 9H), 1.77 (s, 3H), 2.01 (s, 1H), 4.25 (d, *J*= 6.1 Hz, 2H), 5.74 (tq, *J*= 6.1, 1.7 Hz, 1H); ^{13}C NMR 3.37, 8.86, 16.62, 59.14, 136.71, 139.07.

***Z*-26:** IR (neat) 3325, 2951, 2873, 1462, 1070, 1005, 702; ^{1}H NMR 0.79-0.97 (m, 6H), 0.97-1.11 (m, 9H), 1.62-1.76 (br s, 1H), 1.86 (s, 3H), 4.08 (d, *J*= 6.9 Hz, 2H), 6.20 (tq, *J*= 6.9, 1.7 Hz, 1H); ^{13}C NMR 5.15, 8.92, 25.46, 62.62, 138.30, 140.49.

(*E*)-3-(Triethylgermyl)pent-2-en-1-ol (*E*-27): IR (neat) 3307, 2958, 2873, 1460, 1427, 1014, 698; ^{1}H NMR 0.78-0.85 (m, 6H), 0.94 (t, *J*= 7.6 Hz, 3H), 0.99-1.05 (m, 9H), 1.47-1.60 (br s, 1H), 2.20 (dq, *J*= 7.6, 0.6 Hz, 2H), 4.26 (d, *J*= 6.1 Hz, 2H), 5.71 (br t, *J*= 6.1 Hz, 1H); ^{13}C NMR 3.95, 8.86, 14.77, 24.27, 58.95, 136.68, 145.47.

***Z*-27:** IR (neat) 3363, 2970, 2877, 1464, 1456, 1011, 702; ^{1}H NMR 0.83-0.92 (m, 6H), 0.99 (t, *J*= 7.4 Hz, 3H), 1.01-1.07 (m, 9H), 1.27-1.33 (br s, 1H), 2.13 (br q, *J*= 7.4 Hz, 2H), 4.23 (d, *J*= 7.1 Hz, 2H), 6.16 (tt, *J*= 7.1, 1.5 Hz, 1H); ^{13}C NMR 5.45, 8.98, 14.39, 31.11, 62.72, 136.74, 146.17.

Preparation of *E*-5a. To an ethereal (3 ml) solution of ***E*-16** (134 mg, 0.65 mmol) was added phosphorous tribromide (0.03 ml, 0.3 mmol) at -20 °C and the reaction mixture was stirred for 14 h. A saturated $NaHCO_3$ aqueous solution (10 ml) was added and the organic materials were extracted with ether (2 × 10 ml), dried ($MgSO_4$), and concentrated under reduced pressure to afford the crude allylic bromide. To a DME (1.5 ml) solution of 2-(trimethylsiloxy)propene (93 mg, 0.65 mmol) was added an ethereal solution of methyllithium (1.5M, 0.45 ml, 0.65 mmol) at 0 °C. After stirring for 60 min, a THF (1 ml) solution of the crude bromide was added to the reaction mixture. It was then warmed up to room temperature and stirred for 2 h. A saturated NH_4Cl aqueous solution (10 ml) was added and the organic materials were extracted with ether (2 × 10 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 95 : 5) to afford ***E*-5a** (12 mg, 7%).

In a similar manner, ***Z*-5a** was obtained. ***Z*-5a:** IR (neat) 3068, 2954, 1718, 1618, 1429, 1250, 1111, 835, 816, 773, 731, 702, 667; ^{1}H NMR 0.39 (s, 6H), 1.81 (s, 3H), 1.97 (s, 3H), 2.10-2.30 (m, 4H), 5.95-6.07 (m, 1H), 7.28-7.38 (m, 3H), 7.45-7.56 (m, 2H); ^{13}C NMR -1.50, 25.07, 26.48, 29.74, 43.33, 127.79, 128.84, 133.67, 134.26, 139.35, 141.74, 208.31.

Preparation of *Z*-5c. To a THF (1.5 ml) solution of diisopropylamine (66 mg, 0.65 mmol) was added a hexane solution of butyllithium (1.6M, 0.41 ml, 0.65 mmol) at 0 °C and the reaction mixture was stirred for 10 min. After cooling to -78 °C, a THF (1.5 ml) solution of cyclohexanone (58 mg, 0.59 mmol) was added with stirring, and the reaction mixture was gradually warmed to 0 °C over 3 h. A THF (1 ml) solution of the crude bromide, prepared from ***Z*-16** (122 mg, 0.59 mmol) and phosphorous tribromide (0.04 ml, 0.3 mmol), was then added to the reaction mixture. After stirring for 1.5 h, a saturated NH_4Cl aqueous solution (10 ml) was added, and the organic materials were extracted with ether (2 × 10 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane-AcOEt, 95 : 5) to afford ***Z*-5c** (36 mg, 22%). ***Z*-5c:** IR (neat) 3070, 2937, 1714, 1616, 1429, 1250, 1126, 1111, 835, 816, 773, 733, 702; ^{1}H NMR 0.38 (s, 3H), 0.40 (s, 3H), 1.04-1.23 (m, 1H), 1.40-2.49 (m, 10H), 1.81 (s, 3H), 6.00-6.12 (m, 1H), 7.29-7.37 (m, 3H), 7.47-7.56 (m, 2H). ^{13}C NMR -1.52, -1.33, 24.90, 25.20, 27.88, 31.57, 33.38, 41.93, 51.09, 127.70, 128.74, 133.70, 134.21, 139.50, 141.65, 212.59.

In a similar manner, both stereoisomers of the δ-silyl and δ-germyl-γ,δ-unsaturated ketones **5** and **28** were prepared using lithium enolates of 2-hexanone or cyclohexanone.

(*E*)-9-(Dimethylphenylsilyl)dec-8-en-5-one (*E*-5b): IR (neat) 3068, 2958, 1716, 1618, 1429, 1248, 1111, 833, 814, 773, 731, 702; ^{1}H NMR 0.31 (s, 6H), 0.90 (t, *J*= 7.3 Hz, 3H), 1.22-1.37 (m, 2H),

1.48-1.69 (m, 2H), 1.67 (s, 3H), 2.32-2.53 (m, 6H), 5.73 (tq, *J*=6.6, 1.8 Hz, 1H), 7.30-7.37 (m, 3H), 7.44-7.51 (m, 2H); ^{13}C NMR -3.51, 13.87, 14.74, 22.35, 22.96, 25.94, 42.07, 42.67, 127.67, 128.82, 133.91, 135.53, 138.45, 139.40, 210.95.

***Z*-5b:** IR (neat) 3070, 2960, 1716, 1618, 1429, 1250, 1111, 835, 816, 775, 731, 702; ^{1}H NMR 0.39 (s, 6H), 0.87 (t, *J*= 7.2 Hz, 3H), 1.14-1.36 (m, 2H), 1.36-1.57 (m, 2H), 1.81 (s, 3H), 2.17-2.26 (m, 6H), 5.95-6.07 (m, 1H), 7.29-7.40 (m, 3H), 7.46-7.59 (m, 2H); ^{13}C NMR -1.47, 13.84, 22.28, 25.06, 25.81, 26.54, 42.35, 42.37, 127.77, 128.82, 133.67, 134.07, 139.40, 141.99, 210.67.

***Z*-5d:** IR (neat) 3070, 2962, 2937, 1716, 1612, 1448, 1429, 1250, 1111, 835, 816, 773, 733, 702; ^{1}H NMR 0.39 (s, 3H), 0.40 (s, 3H), 0.98 (t, *J*= 7.5 Hz, 3H), 1.10 (ddt, *J*= 13.1, 11.9, 3.7 Hz, 1H), 1.42-1.62 (m, 2H), 1.67-1.74 (m, 1H), 1.76-1.84 (m, 1H), 1.84-1.93 (m, 1H), 1.93-2.00 (m, 1H), 2.00-2.09 (m, 1H), 2.09-2.21 (m, 3H), 2.24-2.32 (m, 1H), 2.40 (dt, *J*= 14.7, 6.1 Hz, 1H), 5.99-6.06 (m, 1H), 7.28-7.36 (m, 3H), 7.47-7.55 (m, 2H); ^{13}C NMR -1.14, -1.00, 15.45, 24.92, 27.88, 31.20, 31.65, 33.32, 41.94, 51.07, 127.66, 128.65, 133.80, 139.93, 140.67, 212.61.

(*E*)-9-(Triethylgermyl)dec-8-en-5-one (*E*-28b): IR (neat) 2965, 2875, 1716, 1622, 1464, 1379, 1022, 706; ^{1}H NMR 0.66-0.84 (m, 6H), 0.90 (t, *J*= 7.0 Hz, 3H), 0.84-1.07 (m, 9H), 1.20-1.44 (m, 2H), 1.44-1.63 (m, 2H), 1.72 (s, 3H), 2.29-2.53 (m, 6H), 5.41-5.52 (m, 1H); ^{13}C NMR 3.43, 8.87, 13.82, 16.28, 22.36, 22.70, 25.97, 42.48, 42.65, 136.16, 136.27, 210.93.

***Z*-28b:** IR (neat) 2962, 2875, 1718, 1628, 1464, 1379, 1016, 704; ^{1}H NMR 0.76-0.96 (m, 9H), 0.96-1.10 (m, 9H), 1.20-1.41 (m, 2H), 1.47-1.65 (m, 2H), 1,78 (s, 3H), 2.19-2.49 (m, 6H), 5.91 (tq, *J*= 7.1, 1.5 Hz, 1H); ^{13}C NMR 4.90, 9.01, 13.86, 22.34, 25.52, 25.94, 26.48, 42.66, 43.05, 136.07, 138.15, 210.81.

(*E*)-2-[3-(Triethylgermyl)but-2-enyl]cyclohexanone (*E*-28c): IR (neat) 2954, 2872, 1716, 1624, 1448, 1126, 1022, 706; ^{1}H NMR 0.65-0.88 (m, 6H), 0.88-1.13 (m, 9H), 1.23-1.46 (m, 1H), 1.52-1.95 (m, 3H), 1.71 (s, 3H), 1.95-2.60 (m, 7H),5.40-5.55 (m, 1H); ^{13}C NMR 3.40, 8.82, 16.37, 24.91, 27.81, 33.21, 41.90, 50.75, 53.33, 135.45, 136.49, 212.58.

***Z*-28c:** IR (neat) 2950, 2872, 1716, 1626, 1448, 1126, 1014, 702; ^{1}H NMR 0.71-0.94 (m, 6H), 0.94-1.17 (m, 9H), 1.23-1.47 (m, 1H), 1.53-2.62(m, 10H), 1.79 (s, 3H), 5.85-5.99 (m, 1H); ^{13}C NMR 4.89, 9.00, 25.14, 25.68, 27.97, 31.53, 33.56, 42.11, 51.33, 136.35, 137.69, 212.74.

(*E*)-2-[3-(Triethylgermyl)pent-2-enyl]cyclohexanone (*E*-28d): IR (neat) 2949, 2870, 1713, 1616, 1450, 1126, 1020; ^{1}H NMR 0.72-0.81 (m, 6H), 0.91 (t, *J*= 7.6 Hz, 3H), 0.96-1.03 (m, 9H), 1.26-1.40 (m, 1H), 1.58-1.75 (m, 2H), 1.80-1.92 (m, 1H), 1.97-2.22 (m, 5H), 2.25-2.36 (m, 2H), 2.36-2.44 (m, 1H), 2.52 (dt, *J*= 14.8, 5.3 Hz, 1H), 5.37-5.45 (m, 1H); ^{13}C NMR 4.01, 8.89, 14.38, 23.88, 24.99, 27.61, 27.92, 33.30, 41.99, 50.86, 135.35, 143.04, 212.86.

***Z*-28d:** IR (neat) 2968, 2875, 1716, 1622, 1464, 1128, 1012; ^{1}H NMR 0.82-0.89 (m, 6H), 0.94 (t, *J*= 7.3 Hz, 3H), 0.99-1.04 (m, 9H), 1.29-1.39 (m, 1H), 1.61-1.74 (m, 2H), 1.81-1.91 (m, 1H), 1.96 (dt, *J*= 14.6, 8.2 Hz, 1H), 2.00-2.11 (m, 3H), 2.12-2.19 (m, 1H), 2.25-2.36 (m, 2H), 2.38-2.44 (m, 1H), 2.49-2.58 (m, 1H), 5.84-5.91 (m, 1H); ^{13}C NMR 5.21, 9.10, 15.17, 25.16, 27.97, 31.53, 33.55, 42.13, 51.37, 136.40, 142.71, 212.73.

Preparation of *Z*-19c. To a refluxing ethereal (3 ml) solution of trimethylsilylmagnesium chloride (1.1M, 0.23 ml, 0.25 mmol) was added an ethereal (1.5 ml) solution of ***Z*-5c** (36 mg, 0.13 mmol) and the reaction mixture was refluxed for 1 h. After cooling, saturated NH_4Cl aqueous solution (5 ml) was added and the organic materials were extracted with ether (2 × 10 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was dissolved in THF (1 ml) and added to a THF (2 ml) suspension of potassium hydride (35 wt. % dispersion in mineral oil, 45 mg, 0.39 mmol) at room temperature. The reaction mixture was warmed to 30 °C, and stirred for 1 h. A saturated NH_4Cl aqueous solution (10 ml) was added and the organic materials were extracted with ether (2 × 10 ml), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (hexane) to afford ***Z*-19c** (31 mg, 87%). ***Z*-19c**: IR (neat) 3068, 2931, 1645, 1616, 1429, 1250, 1111, 835, 816, 773, 729, 700; ^{1}H NMR 0.38 (s, 6H), 0.93-1.07 (m, 1H), 1.22-1.44 (m, 2H), 1.47-1.71 (m, 3H), 1.80 (d, *J*= 1.5 Hz, 1H), 1.84-2.03 (m, 3H), 2.08-2.29 (m, 2H), 4.40 (s, 1H), 4.57 (s, 3H), 6.03-6.16 (m, 1H), 7.29-7.37 (m, 3H), 7.46-7.55 (m, 2H); ^{13}C NMR -1.33, -1.28, 24.78, 25.19, 28.69, 33.50, 34.49, 35.34, 43.68, 105.26, 127.70, 128.72, 133.01, 133.74, 139.55, 143.13, 152.59.

In a similar manner, the authentic 1,5-dienes **19** and **20** were obtained.

***Z*-19b:** IR (neat) 3068, 2964, 2939, 1645, 1618, 1429, 1250, 1111, 835, 814, 773, 729, 700; ^{1}H NMR 0.38 (s, 6H), 0.87 (t, *J*= 7.1 Hz, 3H), 1.18-1.40 (m, 4H), 1.79-2.00 (m, 4H), 1.81 (s, 3H), 2.00-2.15 (m, 2H), 4.55 (s, 1H), 4.62 (s, 1H), 6.09 (tq, *J*= 7.1, 1.5 Hz, 1H), 7.28-7.38 (m, 3H), 7.46-7.57 (m, 2H); ^{13}C NMR -1.31, 13.98, 22.42, 25.08, 29.89, 30.71, 35.67, 36.04, 108.67, 127.72, 128.74, 132.62, 133.66, 139.51, 143.71, 149.53.

Z-19d: IR (neat) 3070, 2933, 2856, 1645, 1610, 1429, 1250, 1111, 833, 816, 771, 729, 700; ^{1}H NMR 0.41 (s, 6H), 0.95-1.05 (m, 1H), 0.99 (t, *J*= 7.3 Hz, 3H), 1.29-1.41 (m, 2H), 1.51-1.68 (m, 3H), 1.88-2.01 (m, 3H), 2.09-2.17 (m, 3H), 2.17-2.24 (m, 1H), 4.40 (s, 1H), 4.58 (s, 1H), 6.04-6.12 (m, 1H), 7.30-7.36 (m, 3H), 7.50-7.56 (m, 2H); ^{13}C NMR -1.00, -0.95, 15.56, 24.72, 28.66, 31.20, 33.45, 34.52, 35.27, 43.66, 105.29, 127.65, 128.61, 133.80, 139.38, 139.95, 142.20, 152.56.

Z-20b: IR (neat) 3082, 2968, 1645, 1628, 1464, 1379, 1020, 889, 702; ^{1}H NMR 0.76-0.97 (m, 9H), 0.97-1.10 (m, 9H), 1.24-1.50 (m, 4H), 1.80 (s, 3H), 1.96-2.23 (m, 6H), 4.71 (s, 2H), 5.92-6.03 (m, 1H); ^{13}C NMR 4.94, 9.03, 14.00, 22.47, 25.52, 30.00, 30.73, 35.93, 36.46, 108.66, 134.69, 139.69, 149.79.

Z-20c: IR (neat) 3082, 2960, 2875, 1645, 1626, 1446, 1014, 889, 702; ^{1}H NMR 0.78-0.94 (m, 6H), 0.94-1.09 (m, 9H), 1.09-1.54 (m, 3H), 1.54-1.91 (m, 3H), 1.80 (s, 3H), 1.91-2.14 (m, 3H), 2.19-2.40 (m, 2H), 4.56 (s, 1H), 4.67 (s, 1H), 5.91-6.06 (m, 1H); ^{13}C NMR 4.92, 9.03, 25.05, 25.66, 28.78, 33.67, 34.52, 35.62, 43.77, 105.18, 135.22, 139.07, 152.96.

Z-20d: IR (neat) 3082, 2966, 2875, 1645, 1622, 1446, 889, 789, 702; ^{1}H NMR 0.82-0.89 (m, 6H), 0.95 (t, *J*= 7.5 Hz, 3H), 1.00-1.06 (m, 9H), 1.10-1.19 (m, 1H), 1.19-1.33 (m, 1H), 1.40-1.49 (m, 2H), 1.62-1.75 (m, 2H), 1.78-1.86 (m, 1H), 1.98-2.11 (m, 2H), 1.07 (q, *J*= 7.5 Hz, 2H), 2.23-2.38 (m, 2H), 4.57 (s, 1H), 4.67 (s, 1H), 5.92-5.99 (m, 1H); ^{13}C NMR 5.21, 9.11, 15.27, 25.02, 28.77, 29.70, 31.52, 33.64, 34.49, 35.58, 43.81, 105.23, 137.83, 141.58, 152.92.

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